

VOLUME 3

DECEMBER, 1930

NUMBER 6

NATIONAL
RESEARCH COUNCIL
of CANADA

CANADIAN
JOURNAL OF
RESEARCH



CANADA

*Published under the authority
of the
Chairman of the Subcommittee of the
Privy Council on Scientific and Industrial Research*

OTTAWA • CANADA

CONTENTS

	PAGE
Diffractive Reflection and Scattering of Ultrasonic Waves. Their Influence on Torsion-pendulum Measurements of Sound Intensity— <i>R. W. Boyle and J. F. Lehmann</i>	491
The Influence of Certain Factors on the Output of a Triode Oscillator— <i>Geo. S. Field</i>	510
Methods of Making Lecher-wire Measurements— <i>Geo. S. Field</i>	516
The Detection of Rock Salt by the Methods of Electrical Surveying— <i>T. Alty and S. Alty</i>	521
Molecular Attractive Forces and the Velocity of Chemical Reactions— <i>C. C. Coffin and O. Maass</i>	526
Note on the Effect of Intensive Drying on the Velocity of Gaseous Reactions— <i>C. C. Coffin and O. Maass</i>	540
A Study of the Relative Value of Honey and Sucrose in Bread Manufacture— <i>W. F. Geddes and C. A. Winkler</i>	543
The Bound Water of Wheat-flour Suspensions— <i>R. Newton and W. H. Cook</i>	560

* * *

Publication and Subscriptions

The Canadian Journal of Research is published monthly by the National Research Council of Canada, Ottawa, to which address all correspondence should be directed.

The subscription rate is \$3.00 per year to any part of the world. Single copies are thirty-five cents each.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL of CANADA

VOLUME 3

DECEMBER, 1930

NUMBER 6

DIFFRACTIVE REFLECTION AND SCATTERING OF ULTRASONIC WAVES. THEIR INFLUENCE ON TORSION-PENDULUM MEASUREMENTS OF SOUND INTENSITY¹

BY R. W. BOYLE² AND J. F. LEHMANN³

Abstract

Light waves are too short and ordinary sound waves generally too long to permit experimental work on diffraction and scattering by a single small obstacle. An opportunity for such work however is presented in the case of ultrasonic waves.

This paper describes an experimental investigation on the factors which determine the diffractive reflection and scattering of an ultrasonic wave train by plane circular opaque discs, and discusses the results. These are of special importance in the measurement of sound energy intensity by the torsion-pendulum method, for such measurements should always be corrected to allow for the effect of diffractive scattering of the energy by the measuring-pendulum vane. The correction factor will depend on the size and form of the pendula vanes employed and for circular vanes can be obtained directly from such curves as are shown in this paper as results of the investigation.

Introduction

If a plate or disc in contact with a medium is set into a longitudinal oscillation at right angles to its plane it radiates sonic energy. The distribution of radiated energy depends on the relation between the wave-length of the radiation and the diameter of the source. In the ideal case, if all points of a circular radiating disc, the diameter of which is many times a wave-length, vibrate with the same amplitude and in the same phase, most of the radiated energy will be confined in a beam of angular width 2θ , where $\sin \theta = 1.2\lambda/D$, λ being the wave-length of the energy radiated, and D the diameter of the source. In practical cases there will still be a radiated beam, though this relation may not exactly define it. This is a commonplace of ultrasonic experiments in recent years (5, 6). As D diminishes the source may approximate to a point source, and in the limit, as D becomes extremely small with respect to λ , energy will be radiated equally in all directions.

¹ Manuscript received November 4, 1930.

² Contribution from the Physics Laboratories, University of Alberta, with financial assistance from the National Research Council of Canada. The present paper is an account of work done in 1923.

³ Director, Division of Physics, National Research Council, Canada.

⁴ At the time demonstrator of Physics, University of Alberta, and former holder of a bursary under the National Research Council of Canada.

In the phenomenon of reflection, if a plane wave train is incident normally on a circular disc, it will be reflected at the face of the disc, and one manner of regarding the reflection is to consider the face of the disc as the source of the reflected waves (Huyghen's Principle). The relation between the distribution of the reflected energy and the diameter of the disc should then be the same as the relation between the distribution of energy from a primary source and its diameter. If the diameter of the reflecting obstacle is very large with respect to the incident wave-length, the energy will be reflected directly back on its incident path without much angular spread by diffraction, thus giving the case of normal regular reflection. As the diameter of the reflector diminishes the angular width of the beam in which most of the reflected energy is distributed gradually increases, until the diameter becomes smaller than a wave-length, when, theoretically, the reflected energy is distributed hemispherically, or nearly so. This may be considered to be the case of partial diffractive scattering of energy. As the diameter of the reflecting obstacle further diminishes, the distribution of the reflected energy becomes more diffuse still and approaches a uniform spherical distribution. This should be a condition for complete, or almost complete, scattering.

The type of energy considered in this paper is "ultrasonic", that is, longitudinal, elastic vibrations of ultra-audible pitch and short wave-length. This energy was propagated through water as a medium, its source being an ultrasonic transmitter of a type already described (1). Using energy of this kind an experimental examination of the scattering of a wave train by an opaque disc, of diameter of about one-half to a few wave-lengths, has been made. The resulting information is probably applicable to any type of wave motion, but only in the case of ultrasonic energy can the experiments be performed. The wave-length of light is far too small and that of audible sound too large to permit of an investigation of like nature.

Experiments by many investigators have been carried out on the scattering of light by a large unknown number of minute suspended particles, the sizes of which are not precisely known; it is only the resultant effect due to a very large number of such particles that can be observed. In the present paper, an important effect of the scattering of ultrasonic energy by a single obstacle has been investigated quantitatively, the size of obstacle ranging from about 0.5 to 4.0 wave-lengths in diameter. The reflecting obstacle serves also as the indicating instrument and took the form of a torsion pendulum. Of these, two types were used, the double vane and the single vane, both of which have been previously described (1, p. 85).

The quantitative results obtained have an important practical bearing on a method of absolute measurement of sound energy by torsion pendula; for, from the experimental curves obtained, which show the relation between indicated radiation pressure on a circular reflecting obstacle and its diameter, the best size of pendulum vane can be selected for any energy measurements, and the necessary corrections for this size given.

Method

The method makes use of the phenomenon of pressure of radiation, which is so readily demonstrated in the case of ultrasonic waves and can easily be measured by the torsion-pendulum method. The magnitude of this pressure on an obstacle depends not only on the incident-energy density but also on the distribution of the reflected energy. If the incident energy is reflected directly back on its path, the pressure is a maximum and equal to twice the energy density in the incident wave train. With an increase in the angular width of the zone in which most of the reflected energy is distributed, the component of radiation pressure due to the reflection diminishes and, therefore, the resultant pressure diminishes. When the obstacle is the circular disc of a torsion pendulum, it follows that the torsion in the suspension, required to balance the deflecting torque caused by the radiation, is related to this diffractive reflection and scattering of energy by the vane. The greater this scattering the smaller will be the indicated radiation pressure of the reflected radiation, and in consequence the smaller will be the total torsion in the suspension required to force the vane back to its undisturbed position. It is possible, therefore, in making absolute-energy measurements, for a small pendulum vane to indicate smaller radiation pressure than that which corresponds to the true value of incident-energy density. Since the components of pressure due to normal reflection and scattering depend not only on the size but also on the shape of the reflector, the resultant indicated radiation pressure, as measured by a pendulum vane, will depend on the size and shape of the pendulum employed. The same phenomenon would doubtless be shown in the measurement of the radiation pressure of light waves, if it were not for the fact that the dimensions of the usual reflecting mirrors employed to exhibit the pressures are very large in comparison with the wave-length of the light investigated.

In the work with ultrasonic waves, theoretical considerations and later experiments show that to obtain consistent observations certain important precautions must be observed:

(a) The distribution of the incident energy must be as nearly as possible uniform over the area of the measuring pendulum vane.

(b) The intensity of the incident energy must remain virtually constant during the time, sometimes quite long, necessary for an observation. This necessitates the use of a source of energy of constant or nearly constant emissive power.

(c) The diameter of a measuring pendulum vane must not be too great, for large diameter means a massive pendulum with a long period of natural swing. It was found in the experiments that if this period of oscillation was greater than three minutes, it required at least 30 min. to make a satisfactory observation. (In the present research the ultrasonic frequencies of experiment necessitated a diameter of measuring vane less than 3 cm., about.)

(d) The thickness of the measuring vane must be sufficient to insure practically maximum reflection of the incident waves.

Experimental Details

The ultrasonic generator was mounted at one end of a water tank, previously described (5, p.174), 15 ft. long, 5 ft. wide and 3 ft. deep. The generator was so placed as to radiate its beam horizontally, directly along the middle of the tank. At the other end of the tank hair-felt scattering and dissipating screens (5, p. 174), inclined at an angle of 45° to the end of the tank, were arranged to prevent any backward reflections. A sketch of the general arrangement is shown in Fig. 1.

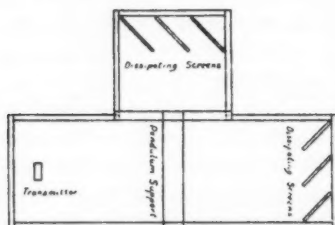


FIG. 1. Plan of experimental tank.

One of the ultrasonic generators used was of the quartz-single metal plate type. Its quartz was a very exceptional single block, 11.5 cm. long, 10.0 cm. wide, and 1.51 cm. thick*, cut from a very large crystal at right angles to an electric axis. A steel plate 1.59 cm. thick was cemented firmly to one face of this block and both were enclosed in a metal case provided with insulated cable and insulating filling in the usual manner. A circular aperture 9.4 cm. in diameter had been cut in the front face of the case and was closed by the quartz block. The whole formed an ultrasonic generator with radiating face of quartz, 9.4 cm. in diameter, directly in contact

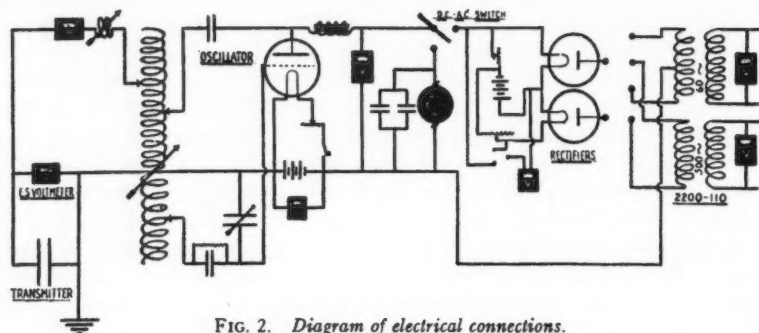


FIG. 2. Diagram of electrical connections.

with the water. Through its attached insulated cable the back steel plate was connected to the high potential side of an electric oscillating circuit operated by electron valves in the usual manner. The high frequencies of this circuit were adjusted by a variable inductance with a variometer for the finer adjustment, and were measured by a Hertzian wave meter. The arrangement is represented in Fig. 2. It was possible to use either a rectified alternating potential, of periodicity either 60 or 500 cycles per second, or a direct continuous potential (up to 2,500 volts) from a direct-current dynamo as the primary electric supply.

*Kindly presented to one of the authors (R.W.B.) by Prof. Paul Langevin of Paris, in 1919.

The torsion pendulum was suspended at a distance from the transmitter. The shortest permissible working distance between the pendulum and transmitter is fixed by the occurrence of regions of maximum and minimum energy distribution, caused by diffraction, in the neighborhood of the transmitter face. In the ideal case simple theory indicates that these interference complications extend in front of the source to a distance d along the axis where $d = \frac{R^2}{\lambda} - \frac{\lambda}{4}$. (R is the radius of the radiating face of the transmitter and λ is the length of emitted waves.) In practical cases the distance d will be something comparable with this. In all the experiments the measuring pendulum vane was placed beyond this region of complication.

All the pendulum vanes used in the experiments were circular in form. Two types of pendulum were selected for the experiments; (a) the double vane, (b) the single "air" vane. These types were employed because many energy measurements in connection with other work were made by means of them. The first type was constructed as follows: Two lead discs of exactly the same diameter and thickness were soldered together at their edges, with their planes at right angles, and suspended by a

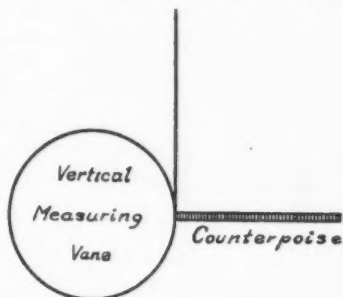


FIG. 3. Double-vane torsion pendulum.

fine phosphor bronze strip attached at the point of contact between the discs. One of the discs hung in a vertical plane and the other in the horizontal, the latter serving merely as a counterpoise for the former, as shown in Fig. 3. The vanes were made of lead because this material was used in other work for certain energy measurements.

The pendulum was placed in the ultrasonic beam so that the vertical vane was central to the beam at right angles to its path. The radiation striking the vane is reflected, and the change in the direction of the energy creates a radiation pressure which deflects the pendulum. On deflection the pendulum is forced back to its zero position by twisting the suspension from the torsion head. This applied torsion will be equal to the deflecting torque which itself is proportional to the radiation pressure on the vane (5, p. 183).

The single-vane pendulum was a modification of the double-vane type, the horizontal counterpoise being omitted. A strip suspension of phosphor bronze, about 90 cm. long, was fixed at top and bottom to a framework and placed under tension. A single circular disc was cemented to one side of this strip which was so arranged as to lie tangentially to the disc. The suspension and pendulum vane were set in a vertical plane, and the vane was placed centrally in the ultrasonic energy field, at right angles to the direction of propagation of the beam. This type of pendulum avoided entirely the effect due to the counterpoise vane of the double-vane type, and in addition had the advantage of giving quicker readings. The arrangement of the torsion pendulum with its mountings and reading device is shown in Fig. 4.

In the preliminary experiments with the single-vane pendulum, a vane of lead was used. It was found that in this case there was a marked gravitational control. The vane set itself in a position of maximum stability from which it

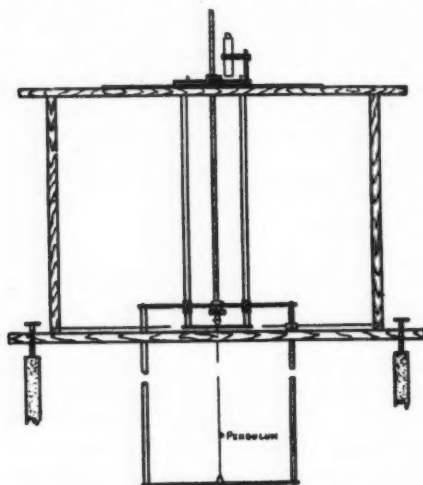


FIG. 4. Pendulum, mountings and support.

could be moved only by the application of a large torque. To overcome this defect a lighter vane was made by cementing thin sheets of mica over the faces of an aluminium ring, and the vane was carefully adjusted for buoyancy until it barely sank in water. A vane of this type gave the discontinuity—water to air—necessary to produce complete reflection of the incident ultrasonic energy, and at the same time reduced the gravitational control forces to a minimum.

The diameter of the pendulum vanes for the present frequencies of experiment could not in practice be much greater than 3 cm. It was found that readings obtained with large massive pendula were

unreliable, because of the disturbances possible within the long period required for oscillation of the pendulum. If the periods of oscillations were greater than three minutes it required at least half an hour to take a satisfactory observation. The necessary generating and control apparatus was sufficiently complex to make it almost certain that within half an hour some slight change would occur sufficient to cause disturbances in the observations.

The thickness of the vertical vane of a pendulum must be sufficient to insure practically maximum reflection. Theoretical considerations show that for a solid vane the best thickness is one-quarter of a wave-length in the material of the vane, but vanes of this thickness would be far too cumbersome and slow. Experimental investigations of the effect of thickness of a solid reflecting partition of lead on the magnitude of the reflected energy (3) have shown that the magnitude of the reflected energy is practically constant for thickness ranging from 0.1 wave-length to 0.45 wave-length. The thickness of the lead vanes used for the double-vane pendula in these experiments was 0.16 cm. The wave-length of the ultrasonic energy ranged from 0.69 cm. to 1.32 cm. (frequencies from 62,400 to 226,000 vibrations per second) so that the thickness of the vanes ranged between 0.12 and 0.23 wave-length. Within this range of vane thickness the reflection from lead is virtually total. No experimental investigation of the relation between the thickness of an air pendulum (hollow vane) and its reflecting power was made; but from theoretical considerations and mathematical calculations, the discontinuity of elastic properties between water and air are so great that such a vane must be a perfect reflector of

ultrasonic energy, unless its thickness happened to be exactly an integral number of half-wave-lengths of the ultra-sound in air. In the present experiments such could not be the case.

Precautions (a) and (b), p. 493, relate to the ultrasonic energy field. This field is dependent only on the ultrasonic transmitter, the frequency of oscillations employed, and on the backward reflection, if any, from the remote walls of the water tank. Particular care was taken to eliminate all such reflections by means of the dissipating screens, so that the transmitter itself and the high frequency voltage imposed on it were the only factors determining the nature of the incident energy field.

The distribution of energy in beams from ultrasonic generators has been carefully investigated (5,p.183). In Fig. 5, energy surveys in horizontal sections of some of the beams used in these experiments are shown. The ordinates are proportional to the energy intensities, and the abscissae represent positions of the centre of the pendulum vane in the energy field, as measured on a line across the beam at right angles to the central axis. From these curves the distribution of energy in the beam is obtained. The energy is at a maximum of intensity at the centre of the beam and rapidly diminishes to zero at the boundary. Only over a small region in the centre

of the beam is the energy distribution approximately uniform. The diameter of this region was about one-tenth of the total diameter of the beam at the sections investigated. In the experiments, great care has to be taken to place the vertical vane of the pendulum in the exact centre of the beam. The area of the vertical vane should not be greater than the area of this central portion of the beam over which the intensity is approximately uniform.

The relation between the emissive power of the transmitter and its frequency of ultrasonic vibration was also investigated. Curves showing this relation have been plotted and are called the "characteristic curve" of the instrument. All transmitters have resonant frequencies and as the frequency of ultrasonic vibration approaches that of resonance the emissive power of the instrument

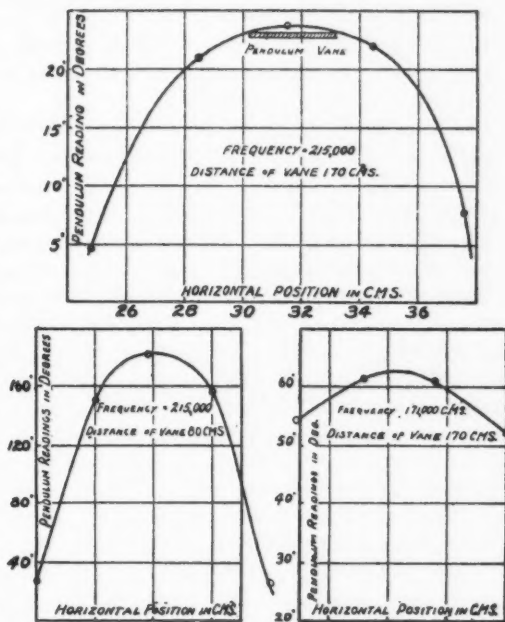


FIG. 5. Energy surveys of ultrasonic beams.

increases rapidly. The characteristic curve of a transmitter used in these experiments is shown in Fig. 6. The curve shows that the resonant peaks are quite sharp. Near the fundamental resonant point a small fluctuation of frequency may diminish the intensity of the emitted energy by from 10 to 50%. As a result it is too difficult to obtain the necessary constancy of energy intensity when operating at or near a resonant frequency. Therefore the experiments were carried out at frequencies lying between two successive resonant frequencies, where the energy emission, though not exactly a minimum, could be kept about constant by means of the available frequency adjustments.

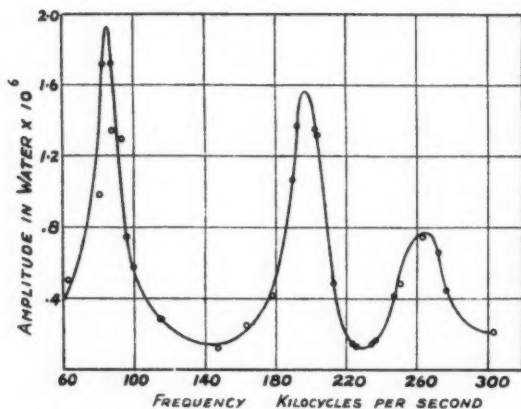


FIG. 6. Emission characteristics of transmitter.

It was generally possible to find a working range at which frequency fluctuations of 2% produced less than 1% change in the emission from the instrument. At these frequencies only relatively small energy intensities were emitted, consequently the imposed high frequency voltage had to be kept fairly high. The smaller energy intensity at such frequencies greatly increased the experimental difficulties of the investigation. During the course of an experiment the high frequency voltage applied to the transmitter was of course kept constant and generally these voltages were from 3000 to 4000 volts.

When the working frequency in an experiment had been established, the next step was to locate the central axis of the ultrasonic beam. The pendulum was placed in various horizontal positions in a cross section of the beam at right angles to its axis and the resulting deflections noted. In this way the position horizontally at which the pendulum reading was a maximum was located. Readings were next taken as the pendulum was moved in a vertical line through this position of horizontal maximum. The maximum readings now gave the exact position of the centre of the beam in the section investigated. Curves showing these beam sections are given in Fig. 5. An examination of these surveys showed the area about the central axis of the beam over which the ultrasonic energy was most uniformly distributed. If this area were not as great as the area of the largest vane to be used the pendulum was moved further away from the transmitter and the process repeated.

It was sometimes possible to find a position for the pendulum at which readings for a given frequency could be obtained with all the vanes employed in an experimental series from the smallest to the largest, but in other cases

the available energy intensity was insufficient to permit of this convenience. Frequently, at the distance necessary to ensure the required uniformity of energy distribution over the larger vanes, the energy intensity was too small to obtain a satisfactory reading with the smaller vanes. When this was the case two series of readings were taken, at different distances from the transmitter. The small pendula were placed fairly close to the source, about 70 or 80 cm. away, and the larger about 170 to 200 cm. away, in all cases the area of uniform energy distribution being sufficient to cover the largest vane used in the series. To correlate the observations with the smaller vanes, taken near the transmitter, with those of the larger, taken further away, the largest vane used in the first series was again used as the smallest vane in the second series, thus making this vane serve as a standard and connecting link for the two series of observations to which all readings could be reduced.

Theoretical Details

An inspection of the energy curves of Fig. 5 will show that the energy intensity in the central portion of the beam, *viz.* that part spanned by the measuring vane, is nearly constant, the values at the edge of the vane even with the largest pendulum employed being never more than 3 to 4% less than at the centre. Suppose therefore that the measuring vane lies in a uniform field of energy density E ergs per cc. If the vane were large enough in area to reflect the incident energy directly back on its path the radiation pressure on the vane would be $2E$ dynes per square centimeter. If we call the average radiation pressure p_a , then under the given conditions $p_a = 2E$.

This radiation pressure acting on the vertical vane produces a torque tending to rotate the vertical vane about the axis of suspension, and the value of this torque can readily be calculated. The area of the vertical vane is πr^2 sq. cm., where r is the radius of the vane, so that the deflecting force acting over the face of the vane is $\pi r^2 p_a$ dynes. The centre of pressure on the vertical vane is the centre of the vane, and therefore the torque (T_v) about the axis of the suspension is $T_v = \pi r^3 p_a$.

In the case of the double-vane pendula, the incident energy also strikes the edge of the horizontal counterpoise and produces a deflecting torque opposing the torque on the vertical vane. The deflection of the pendulum will be due to the resultant of these two. When the incident energy strikes the edge of this horizontal vane, it strikes a curved cylindrical surface and so is reflected in all directions in a horizontal plane. But the thickness of the horizontal vane is only about 0.2 wave-length and therefore incident energy impinging on it will be considerably scattered in a vertical plane. Consequently, as a first approximation, we assume that the radiation pressure on the counterpoise vane due to its reflection is negligible, and consider that the pressure on this vane is due only to the stoppage of the incident energy (2, 3), and this can be computed.

The energy survey curves show that over the counterpoise vane the energy intensity varies, according to the frequency employed and the size of the vane used, from 0.98 to 0.96 of the maximum intensity at the inner edge down to

various values as low as 0.60 of the maximum intensity at the outer edge of the counterpoise vane. Calling k the ratio of the average pressure on this vane to the maximum pressure on the measuring vane, the appropriate value of k can be found from the energy curve for any particular experiment. Its value varies from 0.84 to 0.94 according to the frequency, the size of pendulum vane, and distance of vane from the transmitter. Hence the average pressure over the counterpoise vane may be taken as $k p_a$, acting over an area $2rt$, where t is the vane thickness. The distance of the centre of pressure from the suspension is r , therefore the torque (T_h) on the horizontal vane is

$$T_h = \frac{2r^2 t k p_a}{2} = k r^2 t p_a$$

Therefore the resultant deflecting torque on the pendulum is

$$T_v - T_h = p_a (\pi r^3 - ktr^2)$$

When the pendulum is balanced at right angles to the direction of the incident energy by the torsion in the suspension, this torsion and the deflecting torque must be equal and opposite. Calling the torsion constant of the suspension C , and the twist on the suspension measured in radians δ , then

$$C \delta = p_a (\pi r^3 - ktr^2)$$

$$\text{or } p_a = \frac{C}{\pi r^3 - ktr^2} \delta$$

It follows that $\delta = \left(\frac{\pi r^3 - ktr^2}{C} \right) p_a$, or δ , which is the pendulum reading, is proportional to the average radiation pressure on the measuring vane.

For the single-vane pendulum t is zero, hence $ktr^2 = 0$ and $p_a = \frac{C}{\pi r^3} \delta$.

As explained in the introduction to this paper, the very large vanes will show the greatest indicated radiation pressure, equal (ideally) to twice the energy density in the incident beam; but as the diameter of the vane decreases the energy is more diffused by diffraction and scattering and the indicated radiation pressure diminishes. Let this greatest possible radiation pressure be P_m . The experimental procedure was to observe the pendulum reading δ for various vanes of different diameter and, from the observations so obtained calculate the corresponding value of p_a . The maximum radiation pressure P_m will be yielded by the vane (say of radius r_m) giving the greatest pendulum reading δ_m .

From the relation above if p_a is the indicated pressure yielded by a vane of radius r which will give a deflection δ ,

$$p_a = \frac{C}{\pi r^3 - ktr^2} \delta, \quad \text{and } P_m = \frac{C}{\pi r_m^3 - k_m t r_m^2} \delta_m$$

$$\frac{p_a}{P_m} = \left(\frac{\pi r_m^3 - k_m t r_m^2}{\pi r^3 - ktr^2} \right) \cdot \frac{\delta}{\delta_m}$$

As only this ratio of radiation pressures is required, the value of the torsion constant of the suspension is immaterial, provided the same suspension is used for all the vanes. It is necessary to know it, however, for the interest of deducing what the radiation pressures actually were in these cases. The highest indicated radiation pressure in any one set of experiments, *i.e.* with

any one frequency and any one distance of vane from the transmitter, has been denoted in the tables following by p_0 . The greatest radiation pressure it was possible to obtain is P_m .

Experimental Observations and Results

Five series of experiments were carried out with double-vane pendula. For two sets the frequency of the incident ultrasonic energy was 215,000 cycles per second; for the three others the frequencies were respectively 171,000, 120,000 and 112,000 cycles per second. The ultrasonic wave-length could be calculated from the frequency, from the fact that the velocity of the ultrasonic energy in the water of the tank at the temperature of these experiments, *viz.*, 15°C., was 1.48×10^5 cm. per second (4).

In the experiments carried out at 120,000 cycles per second, only two sets of readings were taken, for the transmitter broke down before this series could be completed. When the experiments were carried out at a frequency of 112,000 cycles per second, the largest vane used had a diameter equal to 0.96 wave-length. The results obtained in the first four series had shown that when the diameter of vane is 0.95 wave-length the pressure of radiation is 0.48 of the maximum pressure obtained with large vanes. Consequently in the series at the frequency of 112,000 cycles per sec., the relative radiation pressures were calculated on the assumption that the relative pressure was 0.48 for the vane of diameter 0.96 wave-length. The suspension used in the double-vane experiments was a fine strip of phosphor bronze 80 cm. long. The torsion constant of this suspension was found to be 0.0040 C.G.S. units.

A suspension occasionally broke and was replaced from the same spool of phosphor bronze. As a result the torsion constant was not exactly the same for all suspensions, the variation being about 10%. However, care was taken to preserve the same suspension for all readings in any one series, and as it is the relative radiation pressure in any one series with which we are concerned, the exact value of the torsion constant was immaterial.

A. Results with Double-vane Pendulum

TABLE I
RESULTS OBTAINED WITH DOUBLE-VANE PENDULUM IN FIRST SERIES OF EXPERIMENTS

D cm.	D/ λ	δ Radians	P_a Dynes/cm ²	P_a/P_0
2.50	3.62	2.09	0.00145	1.00
1.88	2.72	0.88	0.00140	0.97
1.51	2.18	0.435	0.00137	0.95

NOTE:— Frequency of vibration, 215,000 cycles per second.
 Ultrasonic wave-length, 0.69 cm.
 Distance of pendulum from transmitter, 170 cm.
 Maximum radiation pressure, $p_0 = 0.00145$ dynes per sq. cm.

TABLE II

RESULTS OBTAINED WITH DOUBLE-VANE PENDULUM IN SECOND SERIES OF EXPERIMENTS

D cm.	D/ λ	δ Radians	P_a Dynes/cm ²	P_a/P_0
1.88	2.72	5.01	0.0080	0.95
1.50	2.17	2.36	0.0075	0.90
1.27	1.83	1.46	0.0079	0.94
1.00	1.45	0.75	0.0084	1.00
0.80	1.16	0.27	0.0062	0.74

NOTE:— Frequency of vibration, 215,000 cycles per second.
 Ultrasonic wave-length, 0.69 cm.
 Distance of pendulum from transmitter, 80 cm.
 Maximum radiation pressure, $P_0 = 0.0084$.

TABLE III

RESULTS OBTAINED WITH DOUBLE-VANE PENDULUM IN THIRD SERIES OF EXPERIMENTS

D cm.	D/ λ	δ Radians	P_a Dynes/cm ²	P_a/P_0
3.25	3.74	12.10	0.00413	0.93
2.50	2.88	6.46	0.00446	0.99
1.88	2.16	2.66	0.00425	0.95
1.50	1.73	1.43	0.00450	1.00
1.27	1.46	0.81	0.00440	0.98
1.00	1.15	0.25	0.00281	0.63

NOTE:— Frequency of vibration, 171,000 cycles per second.
 Ultrasonic wave-length, 0.87 cm.
 Distance from transmitter, 170 cm.
 Maximum radiation pressure, $P_0 = 0.0045$.

TABLE IV

RESULTS OBTAINED WITH DOUBLE-VANE PENDULUM IN FOURTH SERIES OF EXPERIMENTS

D cm.	D/ λ	δ Radians	P_a Dynes/cm ²	P_a/P_0
3.25	2.62	1.85	0.00062	1.00
1.50	1.21	0.16	0.00050	0.80

NOTE:— Frequency of vibration, 120,000 cycles per second.
 Ultrasonic wave-length, 1.24 cm.
 Distance of pendulum from transmitter, 200 cm.
 Maximum radiation pressure, $P_0 = 0.00062$.

TABLE V

RESULTS OBTAINED WITH DOUBLE-VANE PENDULUM IN FIFTH SERIES OF EXPERIMENTS

D cm.	D/ λ	δ Radians	p_a Dynes/cm ²	p_a/p_o
1.27	0.96	0.680	0.00369	0.48
1.00	0.76	0.286	0.00321	0.41
0.80	0.60	0.112 to 0.073	0.00259 to 0.00167	0.34* to 0.21
0.60	0.45	0.037 to 0.025	0.00216 to 0.00145	0.28 * to 0.19

NOTE:— Frequency of vibration, 112,000 cycles per second.

Ultrasonic wave-length, 1.32 cm.

Distance of pendulum from transmitter, 150 cm.

* as ascertained by extrapolation from the results quoted in Tables I to IV that when $D/\lambda = 0.96$, the value of $p_a/p_o = 0.48$.

*It was very difficult to obtain accurate results with these small double-vane pendula and relatively wide angle beam.

Plotting the curves for these series of p_a/p_o with respect to D/λ , fitting them together and correlating to a common standard, the ratios p_a/P_m are found for the construction of the final curve, Fig. 7, and of the final Table VI. The dotted portion of the curve indicates the less accurate and most uncertain part.

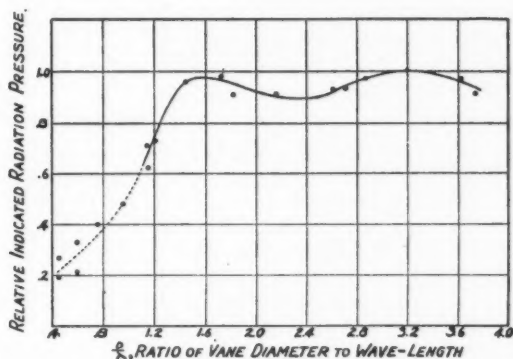
FIG. 7. Relation of indicated radiated pressure to $\frac{D}{\lambda}$ for double-vane pendula.

TABLE VI

VALUES OBTAINED WITH DOUBLE-VANE PENDULA CORRELATED TO A COMMON STANDARD

D/ λ	Correlated p_a/P_m for curve 7	D/ λ	Correlated p_a/P_m for curve 7
3.74	0.91	1.46	0.96
3.62	0.97	1.21	0.73
3.20	1.00	1.16	0.71
2.88	0.97	1.15	0.62
2.72	0.93	0.96	0.48
2.62	0.93	0.76	0.40
2.17	0.91	0.60	0.33 to 0.21
1.83	0.91	0.45	0.27 to 0.19
1.73	0.98		

B. Results with Single-vane Pendulum

Four series were taken with single air vane pendula, two at a frequency of 120,400 cycles per second, one at 226,000 cycles per second, and one at 62,900 cycles per second. The total length of the suspension used in the pendulum frame was 90 cm., the vane being fixed 60 cm. from the top end. The torsion constant of the suspension was 0.0053 C.G.S. units.

TABLE VII

RESULTS OBTAINED WITH SINGLE-VANE PENDULUM IN FIRST SERIES OF EXPERIMENTS

D	D/ λ	δ Radians	p_a Dynes/cm ²	p_a/p_o
1.01	1.54	0.47	0.0062	1.00
2.03	3.10	3.20	0.0052	0.80
2.58	3.94	7.40	0.0061	0.99

Frequency of vibration, 226,000 cycles per second.

Ultrasonic wave-length, 0.655 cm.

Distance from transmitter, 172 cm.

Maximum pressure, $p_o = 0.0062$.

TABLE VIII

RESULTS OBTAINED WITH SINGLE-VANE PENDULUM IN SECOND SERIES OF EXPERIMENTS

D	D/ λ	δ Radians	p_a Dynes/cm ²	p_a/p_o
1.01	0.82	0.18	0.0024	0.73
1.52	1.24	0.86	0.0033	1.00
2.58	2.10	3.05	0.0024	0.73

Frequency of vibration, 120,400 cycles per second.

Ultrasonic wave-length, 1.23 cm.

Distance from transmitter, 70 cm.

Maximum pressure, $p_o = 0.0033$.

TABLE IX

RESULTS OBTAINED WITH SINGLE-VANE PENDULUM IN THIRD SERIES OF EXPERIMENTS

D cm.	D/ λ	δ Radians	p_a Dynes/cm ²	p_a/p_o
1.52	1.24	0.23	0.00089	1.00
2.03	1.65	0.50	0.00082	0.93
2.58	2.10	0.82	0.00065	0.73
4.02	3.27	3.66	0.00069	0.78

Frequency, 120,400 cycles per second.

Ultrasonic wave-length, 1.23 cm.

Distance from transmitter, 133 cm.

Maximum radiation pressure, $p_o = 0.00089$.

TABLE X

RESULTS OBTAINED WITH SINGLE-VANE PENDULUM IN FOURTH SERIES OF EXPERIMENTS

D cm.	D/ λ	δ Radians	p_a Dynes/cm ²	p_a/p_0
1.01	0.43	0.09	0.0012	0.34
1.52	0.64	0.49	0.0019	0.54
2.03	0.86	2.15	0.0032	0.91
2.58	1.10	4.48	0.0035	1.00
4.02	1.70	15.9	0.0033	0.95

Frequency, 62,400 cycles per second.

Ultrasonic wave-length, 2.36 cm.

Distance from transmitter, 80 cm.

Maximum radiation pressure, $p_0 = 0.0035$.

From these series, as in the former case, the final correlated values of the ratio p_a/P_m were obtained for Fig. 8 and Table XI. The dotted portion of the curve is the part not covered by experimental observation.

Discussion

The final curves are of the same type though they differ somewhat from one another. Such difference should be expected owing to the effect of the counterpoise of the double-vane pendulum acting both in reflection and diffraction of the incident energy, and it has already been pointed out that the ratio p_a/P_m must depend not only on the size but also on the shape of the pendula. In

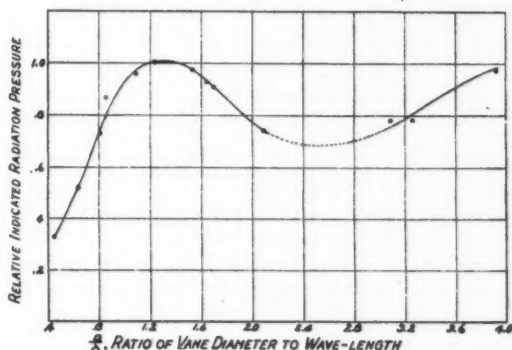
FIG. 8. Relation of indicated radiated pressure to $\frac{D}{\lambda}$ for single-vane pendula.

TABLE XI

VALUES OBTAINED WITH SINGLE-VANE PENDULA CORRELATED TO A COMMON STANDARD

D/ λ	Correlated p_a/P_m for curve 8	D/ λ	Correlated p_a/P_m for curve 8
3.94	0.97	1.24	1.00
3.27	0.78	1.10	0.96
3.10	0.78	0.86	0.87
2.10	0.73	0.82	0.73
1.70	0.91	0.64	0.52
1.65	0.93	0.43	0.33
1.54	0.98		

both curves there is a maximum indicated radiation pressure when the diameter of the vane is about 1.4 wave-length. For diameters less than 1.4 wave-length, in the case of the double-vane pendula, and 1.2 wave-length for the single vanes, the indicated radiation pressure decreases rapidly as the diameter decreases. For diameters larger than 1.4 and 1.2 wave-length respectively, there is a fall and rise in the indicated pressure. The curves may thus be divided into two portions which may be considered separately.

For the smaller pendula, the diminution in indicated radiation pressure with diminishing diameter is undoubtedly due to the scattering effects outlined in the introduction to this paper and in what follows. The fluctuation for the larger pendula may be explained in this same way, but it is possible that further explanation may also be made on the principles that govern the bright spot diffraction phenomenon in an optical shadow. It is anticipated that a later communication will follow on this subject.

The difference between the single and double-vane series, for small pendula of diameter less than 1.2λ , will be due in part to differences in the distribution of the incident and reflected energy in these two cases, owing to the effect of the horizontal vane. The radiation pressure on this counterpoise vane produces a torque the exact magnitude of which is not easily calculated. In this paper a correction has been applied to allow for this torque but the correction was based on simple approximations. For large pendula the correction would be only a small fraction of the actual reading, but with vanes of small diameter the area of the edge of the counterpoise is comparable with that of the face of the vertical vane on which measurements are based. As a result, the computations of the radiation pressure acting on a small double-vane pendulum may be subject to a systematic error of appreciable magnitude.

But undoubtedly with both types of pendulum diffractive scattering will mostly explain the portions of the experimental curves which refer to diameters small in comparison with a wave-length. As yet no mathematical analysis applicable to this part of the problem has been developed, but some general qualitative conclusions may be deduced. Irrespective of the size of the disc or the pendulum vane, there should always be a pressure due to the impact of the incident energy. As the diameter of the disc increases there is an additional pressure due to the concentration of the reflected energy in a beam of angular width, ideally of 2θ , where $\sin \theta = 1.2\lambda/D$. The maximum pressure would occur when the disc reflected all the incident energy back on the incident path, and this maximum pressure would be twice the energy density in the incident wave train. On this hypothesis we should expect the pressure per unit area for a very small vane to be half that for a very large one and also that there would be a gradual increase in the indicated radiation pressure as the diameter of the vanes increased. Fig. 7 and 8 show that, although this factor no doubt contributes to the observed result, it must be considerably modified. The maximum radiation pressure is attained when $D = 1.4 \lambda$ in the double-vane series, and 1.2λ in the single-vane series. For these values of D , $\sin \theta = 0.86$ and 1.00 respectively, which makes $2\theta = 120^\circ$ for the double vanes and 180° for the single vanes. The energy at the boundary of the beam is therefore not

reflected directly back on its path. It has been shown previously that the intensity of the energy at the boundary of a beam is very small in comparison with that at the centre, and this consideration probably has much to do with the above result. It is evident from Fig. 7 and 8 that, when D is equal to about 1.3 to 1.6λ , the pressure due to the resultant effect of both incident and reflected energy reaches a practical maximum. It is also evident that the indicated pressure for small vanes is less than half the maximum pressure and therefore less than the pressure duly expected from the incident energy alone. When D is very small with respect to λ the conditions approximate those of a point source. A point source radiates energy in all directions so that when D is very small the energy striking the disc would be radiated again in practically all directions, behind as well as in front of the disc, the resultant effect being a scattering of the incident energy practically in all directions. It follows that the indicated radiation pressure on a very small obstacle would be less than the pressure due to the incident energy alone on a large disc. Fig. 7 and 8 show that some such effect as this exists, and that there is a gradual gradation from the conditions for a small disc to the conditions for perfect reflection, *i.e.* from a large one.

A rigid mathematical investigation of the problem appears to be extremely difficult. In all mathematical developments of the diffraction theory it is assumed that the wave-length of the energy is extremely small with respect to the dimension of the source. This assumption is justified in any optical application of the diffraction theory, but will not apply here. Mathematical investigations of the scattering of energy, both for light and sound, have been carried out by Lord Rayleigh (8, 9, 10, 11), but the dimensions of the particles he considers are very minute with respect to a wave-length. The small discs used in the present experiments in proportion to the wave-lengths lie between the extremely small particles of Rayleigh and larger obstacles comparable in size with a wave-length to which ordinary diffraction theory may be applied.

On the subject of Rayleigh's analysis, it is interesting to note certain marked discrepancies from the results yielded in the present experiments; though it should be mentioned that the "diffractive scattering" considered in this paper and the "scattering" with which Rayleigh deals are perhaps different phenomena, for Rayleigh assumes that a minute particle in the path of the incident wave in a medium may be considered as equivalent to a change in the density and elastic properties of the medium itself. Referring to a paper by Keen and Porter "On Diffraction of Light by Particles Comparable with a Wave-length" (7), the transmission of light through a suspension of sulphur in a solution of sodium thiosulphate was investigated, and from the paper the following is quoted, "When such a suspension (of sulphur particles) is placed in the path of a beam from an arc lamp, focussed on a screen, the image of the carbon is usually red, of greater or less depth according to the size and number of the diffracting particles. The production of this red color has been satisfactorily explained by Lord Rayleigh as due to selective scattering of blue light by particles which are small compared with a wave-length. One of us noticed, however, that if time be given for the particles to increase in size (and possibly

in number also) the solution after becoming nearly opaque becomes transparent again, but in this new stage an excess of blue is transmitted. This very remarkable result is in direct variance with the current theory of the action of small particles, and presents, therefore, a problem for investigation."

The excess of blue light transmitted by large particles could be explained from the experimental results of the diffractive scattering considered in this paper, if such results could apply. If the size of the particle is fixed, D/λ is smaller for long wave-lengths than it is for short; as a result the long waves are diffractively scattered to a greater extent than are the short and therefore the short wave or blue must predominate in the transmitted light.

Summary

In the experiments here described the factors which determine the diffractive reflection and scattering of an ultrasonic wave train by plane circular opaque discs have been established experimentally. The scattering of energy by discs of diameter of the order of a wave-length is essentially a diffraction phenomenon, and all the observed effects may be explained qualitatively by simple diffraction theory though their mathematical expression is difficult.

The results quoted are of special importance when a torsion pendulum is to be used to measure energy intensities. Such determinations must always be corrected to allow for the effect of the diffractive scattering of energy by the pendulum vane. The necessary correction factor for either double or single-vane pendula will depend on the size and shape of the pendula vanes employed and can be obtained directly from such curves as are shown in this paper.

From these curves, giving the relation between indicated radiation pressure on a circular reflecting obstacle and the ratio of the diameter of the obstacle to the wave-length, the best size of vane of torsion pendulum can be ascertained for use in the quantitative measurement of energy intensity in an ultrasonic train.

Relations of this kind between D/λ and the indicated radiation pressure on the obstacle should be applicable to other types of wave motion, but it is only in the case of ultrasonics that an experimental investigation of the problem can be carried out. The wave-length of ordinary sound is too great, and that of light too small, to permit experimental work on a single obstacle of dimension of the order of a wave-length. Experiments usually are carried out on the scattering of light by a large number of minute particles suspended in a medium in which case it is only the resultant effect due to a very large number of particles that can be observed. In this paper the scattering of energy by a single obstacle has been investigated quantitatively.

References

1. BOYLE, R. W. *Science Progress*, 23:75-105. 1928-29.
2. BOYLE, R. W. and FROMAN, D. K. *Can. J. Research*, 1:405-424. 1929.
3. BOYLE, R. W. and LEHMANN, J. F. *Trans. Roy. Soc. Can.* 21, III:115-125. 1927.
4. BOYLE, R. W., LEHMANN, J. F. and MORGAN, S. C. *Trans. Roy. Soc. Can.* 22, III:371-378. 1928.

5. BOYLE, R. W., LEHMANN, J. F. and REID, C. D. *Trans. Roy. Soc. Can.* 19, III:167-190. 1925.
6. HEHLGANS, F. W. *Ann. Physik*, 86:587-627. 1928.
7. KEEN, B. A. and PORTER, A. W. *Proc. Roy. Soc. London*, (A) 89:370-376. 1913.
8. RAYLEIGH, LORD. *Nature*, 8:319-320. 1873.
9. RAYLEIGH, LORD. *Phil. Mag.* 41:107-120, 274-279. 1871.
10. RAYLEIGH, LORD. *Scientific Papers*, 1:87-103. 1899.
11. RAYLEIGH, LORD. *Theory of Sound*, Macmillan, ed. 1896. p. 296.

THE INFLUENCE OF CERTAIN FACTORS ON THE OUTPUT OF A TRIODE OSCILLATOR¹

BY GEO. S. FIELD²

Abstract

Certain peculiar variations in the radiated energy from a five-metre triode oscillator, observed by a previous experimenter, have been investigated. The factors influencing the output appear to be changes in input and in the surrounding temperature. With tubes employing oxide-coated filaments, these changes are sometimes of considerable importance, while in other cases such variations have a negligible effect. Several curves of output plotted against various input values are given.

Introduction

Some time ago C. H. West (1), working on a wave-length of 5.17 metres, claimed to have observed a considerable change in radiated energy with variations in the intensity of light falling on the transmitter. The radiation was at a maximum in the middle of the day, but decreased in the afternoon and became a minimum when darkness fell; the assumption is that the input was maintained constant during the course of the experiment. He found also that the daylight radiation value could be obtained at night by artificially illuminating the oscillator; so that artificial light and sunlight were equally effective in producing a noticeable change in the radiated energy.

That visible light can have any effect on the output of a triode oscillator seems rather improbable, and the following experiments were conducted to determine if the output variations were not really due to some other disturbing factor, which might or might not have been isolated before.

Experimental

The circuit of the oscillator used is shown in Fig. 1. C is a variable 500 mfd. condenser; L₁ and L₂ are two pieces of copper tubing 0.6 cm. by 86 cm. Later,

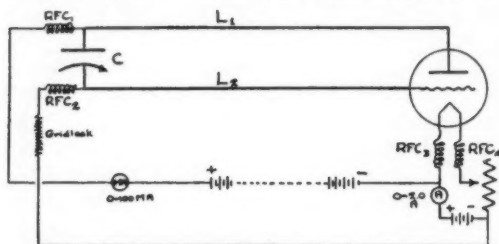


FIG. 1. Diagram of circuit used.

two coils, 8 cm. in diameter and of one and a half turns each, were substituted for the long rods in order to make the transmitter more compact. The radio-frequency chokes were made of 20 turns of No. 26 wire wound on one-inch celluloid forms. The vacuum tube used, a five-watt Northern

Electric 205 D, was operated at the rated filament current of 1.60 amperes and at somewhat less than the rated plate voltage (235 instead of 350). The current was kept constant to within about two one-hundredths of an ampere,

¹ Manuscript received October 15, 1930.

Contribution from the Electrical Engineering Laboratories, University of Alberta.

² Junior Research Physicist, National Research Laboratories; at the time postgraduate student and holder of a bursary under the National Research Council.

and the plate potential to within one volt. By varying the capacity, oscillations could be obtained from 5.0 to 6.5 metres in wave-length with the rods, and from 4.6 to 6.0 metres with the coils. Wave-lengths were measured both on Lecher wires and on a General Radio Company wave meter, the agreement being very good. For an antenna system, two brass rods, each 56 cm. long, were coupled to L_1 and L_2 .

To detect and measure any radiation changes, a loop of wire with a thermogalvanometer in series with it, was placed inductively to the wave meter (Fig. 2), and both wave meter and loop were placed near enough to the aerial system to give a good reading on the galvanometer. Using the wave meter in this way, a good idea was obtained of any change in radiated energy.

Wave meter

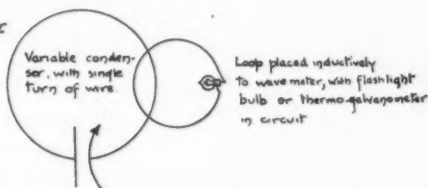


FIG. 2. Device used for measuring relative changes in radiation.

With input variations kept to a minimum, the oscillator was started and readings were taken over periods involving both daylight and dark. At various times a strong beam of light, reflected from a 300-watt incandescent lamp, was turned on the transmitter, and readings again taken. While certain variations did occur in the radiated energy, as much as 15 to 20% in some cases, they did not appear to be related in any way to the intensity of light falling on the transmitter.

Accordingly, it was thought that input variations might be large enough to account for the observed fluctuations in output, and the exact relation between relative output and input was determined. Fig. 3 shows the variation of radiation with filament current in the vicinity of the rated

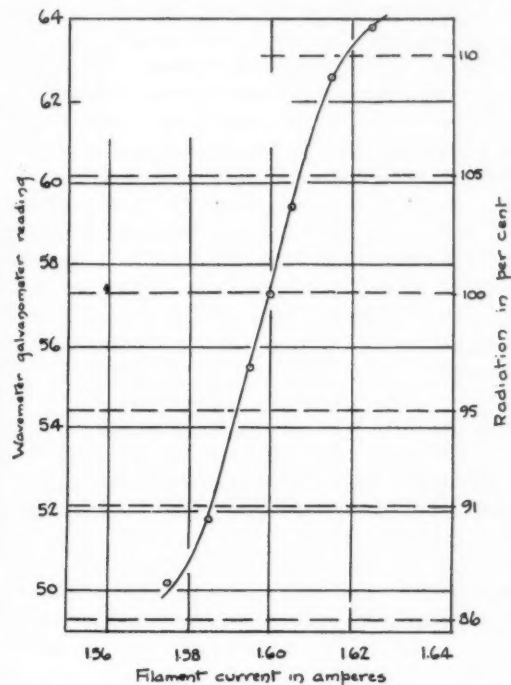


FIG. 3. Variation of radiation with filament current in neighborhood of rated filament current.

filament current value for the tube, and Fig. 4 shows the variation of radiation with plate voltage, in the neighborhood of the operating voltage. It will be noticed that the radiation-filament current curve is very steep, a change of 0.02 ampere from the operating value (1.60 amperes) causing about a 10% change in radiated energy.

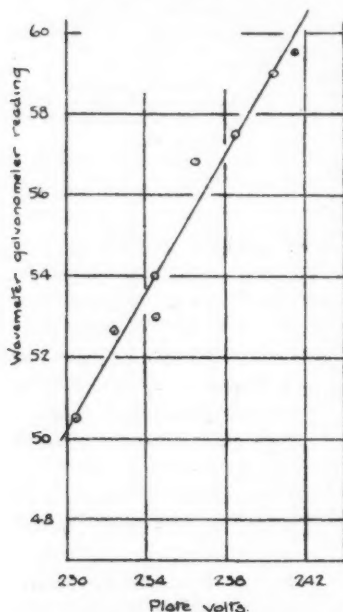


FIG. 4. Variation of radiation with plate voltage in neighborhood of operating voltage.

Since such a small change in filament current caused such a large change in output, variations in the temperature of the surroundings should cause large fluctuations in the output, because the filament temperature is dependent on that of the air about the glass as well as on the current in the wire. Accordingly the temperature of the air was lowered 20° C., with a resulting decrease in radiation of 31%. This is a large change, but in keeping with the sensitivity of the tube to very small filament-current variations.

Two other similar tubes were tried (labelled No. 2 and 3). Whereas the first tube used, No. 1, was comparatively old, No. 2 was somewhat newer, and No. 3 was quite new. These last two tubes were found to be not nearly as sensitive to filament current and environment temperature changes as tube No. 1. Finally, radiation-filament current curves were plotted for each vacuum tube for a wave-length of about five metres, and as it was of interest to observe if frequency had any effect on these curves, similar ones were plotted

for wave-lengths of approximately 80 and 190 metres. For the longer wave-lengths the well-known Hartley circuit was employed. The resulting graphs are shown in Fig. 5, 6 and 7.

With reference to these curves, the following points may be noted:

(a) Each curve has a steep portion, which for the older tubes is at a higher value of filament current; that is, as the tubes with oxide-coated filaments age, a higher temperature is required for a given electron emission. It will be observed that the rated value of filament current (1.60 amperes) for tube No. 1 puts the operating point on a steep part of the curve; for tube No. 2 the operating point is on a less steep portion, and for tube No. 3, a new tube, it is on the flat part of the curve. Hence, only for the new tube does the rated value of current give operation on a part of the curve where small filament temperature changes will make little difference. Even for this tube, at 5.1 metres it is just above the bend.

and the plate potential to within one volt. By varying the capacity, oscillations could be obtained from 5.0 to 6.5 metres in wave-length with the rods, and from 4.6 to 6.0 metres with the coils. Wave-lengths were measured both on Lecher wires and on a General Radio Company wave meter, the agreement being very good. For an antenna system, two brass rods, each 56 cm. long, were coupled to L_1 and L_2 .

To detect and measure any radiation changes, a loop of wire with a thermogalvanometer in series with it, was placed inductively to the wave meter (Fig. 2), and both wave meter and loop were placed near enough to the aerial system to give a good reading on the galvanometer. Using the wave meter in this way, a good idea was obtained of any change in radiated energy.

Wave meter

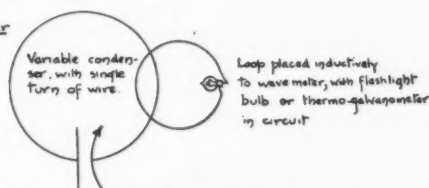


FIG. 2. Device used for measuring relative changes in radiation.

With input variations kept to a minimum, the oscillator was started and readings were taken over periods involving both daylight and dark. At various times a strong beam of light, reflected from a 300-watt incandescent lamp, was turned on the transmitter, and readings again taken. While certain variations did occur in the radiated energy, as much as 15 to 20% in some cases, they did not appear to be related in any way to the intensity of light falling on the transmitter.

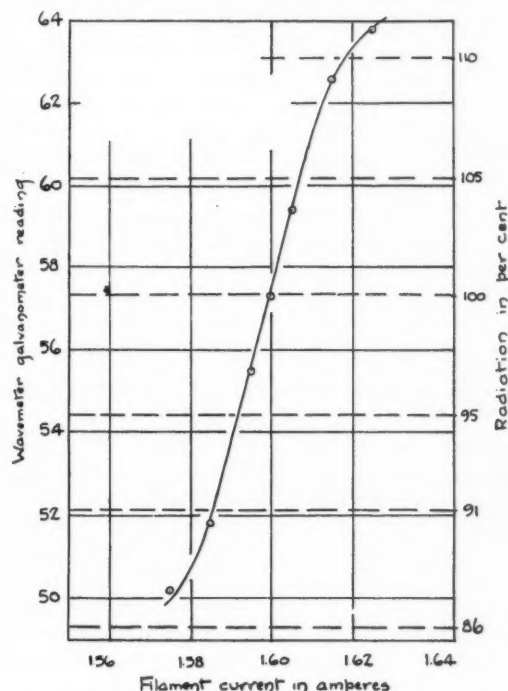


FIG. 3. Variation of radiation with filament current in neighborhood of rated filament current.

Accordingly, it was thought that input variations might be large enough to account for the observed fluctuations in output, and the exact relation between relative output and input was determined. Fig. 3 shows the variation of radiation with filament current in the vicinity of the rated

filament current value for the tube, and Fig. 4 shows the variation of radiation with plate voltage, in the neighborhood of the operating voltage. It will be noticed that the radiation-filament current curve is very steep, a change of 0.02 ampere from the operating value (1.60 amperes) causing about a 10% change in radiated energy.

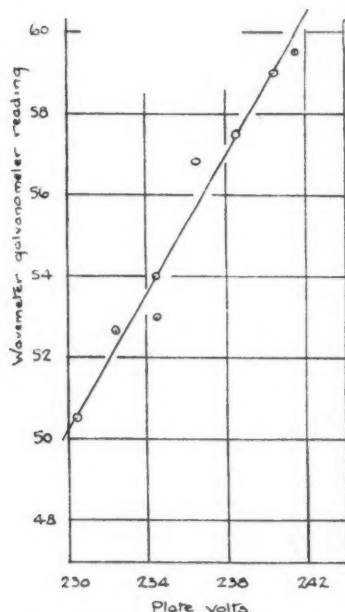


FIG. 4. Variation of radiation with plate voltage in neighborhood of operating voltage.

Since such a small change in filament current caused such a large change in output, variations in the temperature of the surroundings should cause large fluctuations in the output, because the filament temperature is dependent on that of the air about the glass as well as on the current in the wire. Accordingly the temperature of the air was lowered 20° C., with a resulting decrease in radiation of 31%. This is a large change, but in keeping with the sensitivity of the tube to very small filament-current variations.

Two other similar tubes were tried (labelled No. 2 and 3). Whereas the first tube used, No. 1, was comparatively old, No. 2 was somewhat newer, and No. 3 was quite new. These last two tubes were found to be not nearly as sensitive to filament current and environment temperature changes as tube No. 1. Finally, radiation-filament current curves were plotted for each vacuum tube for a wave-length of about five metres, and as it was of interest to observe if frequency had any effect on these curves, similar ones were plotted

for wave-lengths of approximately 80 and 190 metres. For the longer wave-lengths the well-known Hartley circuit was employed. The resulting graphs are shown in Fig. 5, 6 and 7.

With reference to these curves, the following points may be noted:

(a) Each curve has a steep portion, which for the older tubes is at a higher value of filament current; that is, as the tubes with oxide-coated filaments age, a higher temperature is required for a given electron emission. It will be observed that the rated value of filament current (1.60 amperes) for tube No. 1 puts the operating point on a steep part of the curve; for tube No. 2 the operating point is on a less steep portion, and for tube No. 3, a new tube, it is on the flat part of the curve. Hence, only for the new tube does the rated value of current give operation on a part of the curve where small filament temperature changes will make little difference. Even for this tube, at 5.1 metres it is just above the bend.

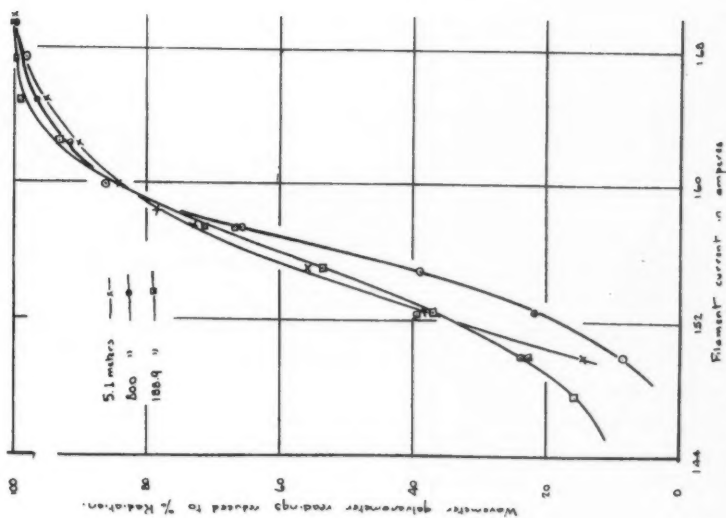


FIG. 5. Variation of radiation with filament current for vacuum tube No. 1.

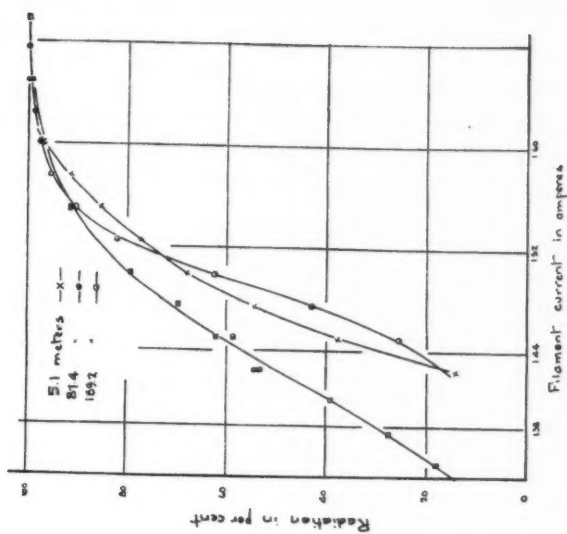


FIG. 6. Variation of radiation with filament current for vacuum tube No. 2.

(b) The shape and position of these curves are not independent of frequency. The 190-metre curves are flatter, and in general show a greater proportion of the 100% radiation value for a given filament current. For some

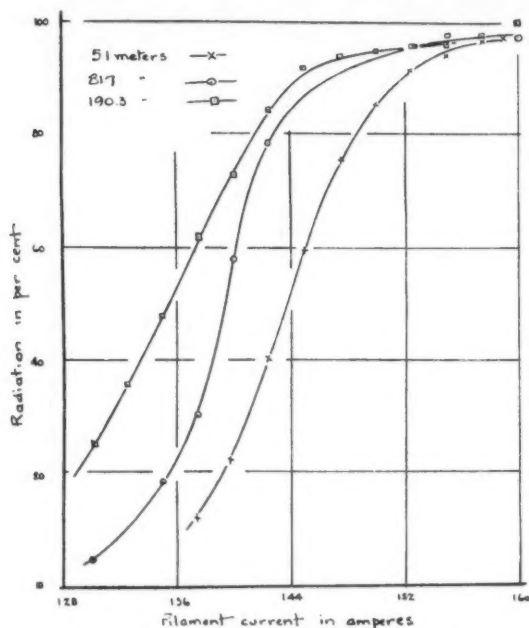


FIG. 7. Variation with filament current for vacuum tube No. 3.

reason, in the 80-metre curves there are steeper points than in any of the other curves. The five-metre curves have a tendency to be concave downward over their whole course, while the other curves each have a point of inflexion.

Summary

1. Contrary to C. H. West's results, light has been found to have no perceptible effect on five-metre radio waves. His results may be explained in two ways:

(a) The importance of input variations was possibly not fully recognized, and he was unwittingly working on the steep part of the radiation-filament current curve.

(b) The temperature of the environment varied considerably, and the result was the same as if the input had fluctuated in value. West's transmitter was probably exposed to sunlight, so that in the middle of the day the temperature and radiation were at a maximum, while towards evening they dropped off to a minimum. This seems probable, since West found that in using arti-

ficial light he had to have a parabolic reflector almost enclosing the oscillator; that is, he had to heat up the vacuum tube to get his supposed "light effects".

2. It has been found that the variation of radiated energy with filament current fluctuations may be very considerable, even when working at the rated value of filament current.

It is thus shown that it is important in certain cases to make sure that the tube is operating on the flat part of the radiation-filament current curve, so that if it is desired to have constant output, it will not be affected to any appreciable extent by slight changes in input.

Acknowledgment

The writer wishes to thank Professor H. J. MacLeod for his help and advice and a number of suggestions which he made during the course of this and other researches.

Reference

1. WEST, C. H. Radio engineering, 1929, p. 53.

METHODS OF MAKING LECHER-WIRE MEASUREMENTS¹BY GEO. S. FIELD²

Abstract

Several methods of measuring the wave-length of electric waves on wires have been investigated. It was found that incorrect results were obtained when neon glow-tubes were moved along the wires to indicate the voltage nodes. By placing the neon lamp at the far end of the wires, however, and using shorting bridges to indicate the nodes, it was found possible to obtain quite consistent results. A thermogalvanometer, used in a similar manner, proved to be a somewhat better indicator and gave results which were more precise.

Introduction

One of the most useful ways of measuring the length of short electric waves is to establish a system of standing waves on two parallel wires, known as Lecher wires (1, 2, 3), and then measure the distance between the nodes of either current or potential. In making such measurements on a wave-length of about five metres, using neon glow-tubes to indicate the potential nodes, the writer observed that serious errors occurred when the tubes were used in certain ways. Another method was then adopted which nullified the disturbing effect of the neon tubes, and with which reasonably accurate results were obtained. Finally, by the use of a thermogalvanometer it was found possible to obtain results in measuring wave-lengths which were accurate to a small fraction of a centimetre.

Experimental

Method 1. The Lecher wires, which were about 10 metres long, were loosely coupled to the oscillator in the ordinary way, and the oscillator started. A neon glow-lamp, made by the General Electric Company, was suspended

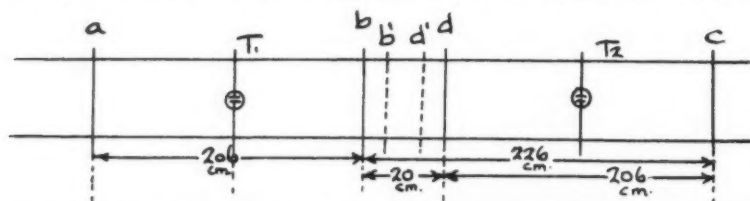


FIG. 1. Diagram showing positions of neon tubes and shorting bridges on the Lecher wires.

from the two wires and moved along them until a potential antinode was reached. The tube then glowed brightly. A piece of wire, forming a short-circuiting bridge, was moved to various positions on the wires. When at the point *a*, Fig. 1, the tube glowed brightly as before. This indicated that *a* was a potential node. Moving the wire a centimetre or less from position *a*

¹ Manuscript received October 15, 1930.

Contribution from the Electrical Engineering Laboratories, University of Alberta.

² Junior Research Physicist, National Research Laboratories, at the time postgraduate student and holder of a bursary under the National Research Council.

caused the tube to cease glowing. A second wire was laid at b and adjusted so that the tube still glowed brightly; b was then also a potential node. Since the antinode, as determined by the glowing tube, was nearly midway between the two nodes a and b , it was assumed that the distance a to b was half a wave-length. This distance was approximately five metres, so the complete wave-length was taken as $2 \times 5 = 10$ metres.

As the circuit used was designed to operate at about five metres, something appeared to be wrong with the Lecher-wire measurements, and they were accordingly repeated.

The tube T_1 was placed at an antinode and point a found as before. This time a was only some 100 cm. from T_1 , whereas previously it had been nearly 250 cm. from the tube. The second point b was found at a distance of 206 cm. from a .

It was decided to use a second neon tube T_2 , which was available, and block off another half-wave-length. Accordingly T_2 was placed as shown, and a third shorting bridge adjusted at a point c . It was then found that whereas distance ab was about 206 cm., distance bc was about 226 cm., both representing, presumably, half a wave-length.

A fourth piece of wire was placed across the two Lecher wires, and when adjusted to the position d , both tubes still glowed steadily. At this stage, therefore, there were shorting wires at a, b, c, d , presumably nodes; and neon tubes at T_1 and T_2 , assumed to be antinodes.

An attempt was then made to bring the wires at b and d together. It was found that the distance bd could be decreased from its original value of about 20 cm. to zero, though moving the wires from b and d made the glow-tubes very unstable. This is to say, if the wires were in some other position (say b' and d'), the voltage at T_1 and T_2 apparently dropped very nearly to the critical voltage of the tube. By "critical voltage" is meant the minimum value which will cause a discharge through the tube.

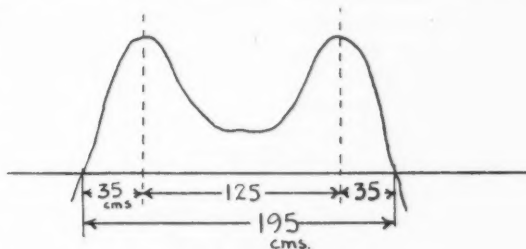


FIG. 2. Voltage distribution along the wires.

An investigation into the voltage distribution along the wires was next attempted. Positions a and b for the shorting wires (tube T_1 as before) were found by adjustment. The second tube and wires c and d were left off. The glow-tube was then moved along the wires, first towards a and then towards b . By estimating the voltage from the brightness of glow of the tube, the general shape of the voltage curve along the wire was plotted (Fig. 2). This and other similar curves are given as an indication only. While the peaks could be definitely established, their distances from the datum line relative to those of the hollows could only be surmised. An examination

of this curve and of the ones in the succeeding figures will show that while none of these curves are pure sine waves, they are of a complex type such

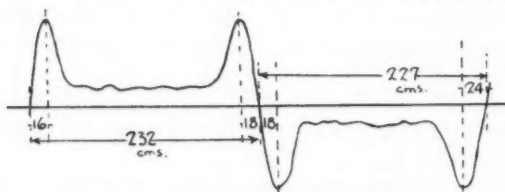


FIG. 3. Voltage distribution along the wires.

as would be formed by a number of the odd harmonics (3rd., 5th., 7th., etc.) impressed on a fundamental sine wave. Whether these harmonics were actually present is not definitely assured, because of the presence of other peculiarities

in the Lecher-wire system, as described in the following paragraph.

On each of three nodes was placed a shorting bridge and each of the two antinodes was examined with a neon tube. The result was a curve such as Fig. 3. In using the three shorting wires and two tubes the distance from node to node was not the same as that obtained with two bridges and one tube. It was observed also that if the nodes were found at some other part of the Lecher-wire system the distance between nodes was different. The results obtained at different points on the wires are shown in Fig. 2, 3 and 4.

These results led to the belief that the neon tubes and shorting bridges might form resonance circuits superimposed on the fundamental Lecher-wire circuit, of such a character that the resulting nodes varied with the part of the Lecher system upon which the extra circuit was imposed.

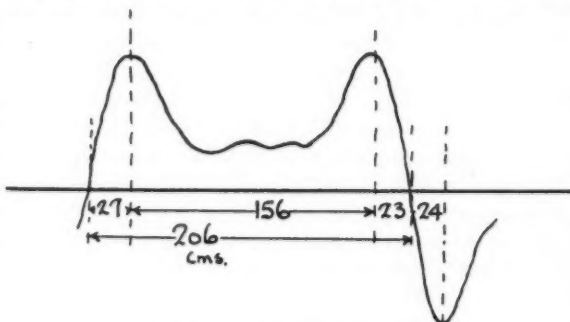


FIG. 4. Voltage distribution along the wires.

That these glow-tubes really had some effect on the system was proved by noting the effect that one glow-tube had on the other. With both tubes far enough off maximum voltage points so that they were glowing unstably, occasionally one tube would cease glowing. It could be started again by discharging on it a small electrostatic charge, generated by the operator sliding on the floor; he would then discharge it on the tube by touching the glass with his finger. As soon as the tube glowed, the second tube would in many cases go out. By starting the second tube in the same manner, the first would likewise cease glowing. That is, the tubes had a reciprocal action.

It was thought that the tubes might be working as condensers, though of course the capacity would be very small. The electrodes in the tubes are semi-cylinders, with a fairly large area; accordingly, to reduce any capacitance

effect, only one of these electrodes was used, and for the other electrode a piece of wire was tied with string to the outside of the bulb, just touching it at the top. Any condenser effect was thus reduced to a negligible quantity. There was no perceptible improvement in the standing-wave system. Therefore any effect that the tubes have on the oscillations must be due to their conducting properties.

Method 2. One of the glow-tubes was connected at the end of the Lecher wires. Assuming that the neon tube did affect the standing waves on the wires, by placing it on the end a constant end effect was introduced, which should not have changed the length of the waves on the rest of the wires.

Using the shorting bridges as before, points, or nodes were found where the presence of these bridges did not cause the tube to cease glowing. By this method it was found possible to place the bridges accurately to within one or two centimetres. A sample of the readings obtained is as follows:

$$\text{Distance between 1st. and 2nd. node } \left(\frac{\lambda}{2}\right) = 254 \text{ cm.}$$

$$\begin{array}{l} \text{Distance between 2nd. and 3rd. node } \left(\frac{\lambda}{2}\right) = 252 \text{ cm.} \\ \hline \lambda = 506 \text{ cm.} \end{array}$$

It will be noticed that this wave-length is considerably greater than would be indicated by the results of Method 1, and is a further indication of the disturbing effect of the glow-tubes when placed between the shorting bridges.

Method 3. It was thought that greater accuracy might be obtained by replacing the glow-tube by a thermogalvanometer. Accordingly, a galvanometer was connected across the far end of the wires. In this case, adjusting a shorting bridge to a nodal point caused an abrupt rise in galvanometer current. This rise was so sudden that the bridge was easily placed to an accuracy of a millimetre. The position of the bridge was noted, and a second node was found with the bridge as before. Four of these points were found, and the half wave-lengths, as measured on the wire, all agreed to a small fraction of a centimetre.

This method was by far the most accurate of the three, and measurements which were later made on a General Radio Company wave meter checked exactly with those made on the Lecher wires using the thermogalvanometer.

Summary

Several methods of making Lecher-wire measurements have been described, and it has been shown that no reliance can be placed on the method which uses one or more neon lamps, placed between shorting bridges, to indicate the potential nodes. Apparently the neon tubes absorb so much energy that they become sources of reflection themselves, and hence cause additional standing waves to be superimposed on the original standing-wave system.

The method which utilizes a galvanometer at the far end of the wires appears to be the best of those described.

Acknowledgment

The writer wishes to thank Professor H. J. MacLeod for his help and advice and a number of suggestions which he made during the course of this and other researches.

References

1. FLEMING, J. A. Principles of electric wave telegraphy and telephony, p. 320. Longmans, New York, 1919.
2. KRUSE, R. S. QST., p. 13, October, 1924.
3. STARLING, S. G. Electricity and magnetism for advanced students, p. 458. Longmans, New York, 1920.

THE DETECTION OF ROCK SALT BY THE METHODS OF ELECTRICAL SURVEYING¹

BY T. ALTY² AND S. ALTY³

Abstract

Experiments on the detection of rock salt deposits by electrical methods are described. It is shown that these methods give definite indications of the depth of the deposit when the latter is as much as 600 ft. below the surface.

The interpretation of results obtained by the "single electrode probe" method is discussed.

Introduction

During the past summer the methods of electrical surveying have been used in England to determine the depth of rock salt deposits and for other purposes. Since little work on the application of these methods to substances such as salt appears to have been published, the results obtained may be of interest and are given in this note.

The geological structure of the field on which the experiments were performed is comparatively simple and is known in considerable detail from the records of borings made at a number of points on the field. Beneath a surface covering of drift, four or five hundred feet of marl overlie the rock salt, which extends downward for several hundred feet below the marl. The rocks are almost horizontal with a slight dip to the south west; the marl varies in water content but appears to be fairly uniform in structure throughout.

To extract the salt a borehole is usually constructed to extend almost to the bottom of the salt deposit. Water is passed down this hole and, after dissolving the rock salt at the bottom, flows up a return pipe to the surface as brine. In this way a cavity filled with brine is formed at the base of each borehole and this cavity increases in volume as more and more salt is removed.

The experiments described were undertaken with the object of obtaining:

- (a) an estimate of the depth of the upper surface of the rock salt,
- (b) an estimate of the depth of the upper surface of the brine cavities at the base of the boreholes.

Method

The "single electrode probe" method, as described by Eve and Keys (1), was used. In this method an electrode *A* (Fig. 1) is placed in the ground over the point to be explored and another electrode *B* is inserted at a considerable distance from *A*. A battery is then connected to *A* and *B* so that a current flows through the ground between them.

If this ground is uniform and the distance *AB* is sufficiently great, the equipotentials about *A* will be approximately hemispherical as shown in Fig. 1.

Measurements of the total current *i* in the circuit and the potential difference *V* between any two equipotentials of radii *R*₁ and *R*₂, render it possible to

¹ Manuscript received October 30, 1930.

² Professor of Physics, University of Saskatchewan, Saskatoon, Canada.

³ Research Physicist, England.

obtain the average resistivity ρ of the ground between these equipotentials, as follows:

Let $AC = R_1$, and $AD = R_2$.

Then the total resistance between the equipotentials through C and D ,

$$= S = \frac{V}{i} = \int_{R_1}^{R_2} \frac{\rho dr}{2\pi r^2} = \frac{\rho}{2\pi} \left(\frac{1}{R_1} - \frac{1}{R_2} \right)$$

Hence

$$\rho = \frac{2\pi V}{i \left(\frac{1}{R_1} - \frac{1}{R_2} \right)} \quad (1)$$

If, on the ground, a straight line passing through A is divided up into steps and the potential between successive steps is measured, then ρ for each step can be determined from equation (1). Suppose now that a good conductor occurs at the level XY . Then the average resistivity between the equipotentials D and E which intersect

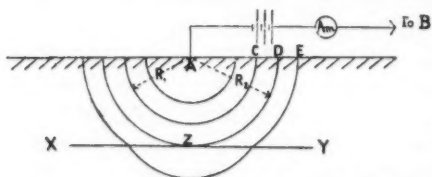


FIG. 1. Diagram illustrating the single electrode probe method of electrical surveying.

the conductor will be decreased and the voltage between D and E will be lower than normal. This decrease in voltage will first appear at a point D such that $AD = AZ$ so that the depth of the conductor may be inferred from the distance AD at which the decrease in voltage, and therefore in ρ , first appears.

In practice therefore the potential difference between successive equal intervals on the ground surface is determined and ρ for each step is calculated by equation (1). The resistivity so obtained is plotted against d , the distance from the potential electrode to the central electrode.

If a good conductor were present below A the resulting graph should show a sudden decrease in ρ at a value of d equal to the depth of the conductor.

Experimental

In our experiments porous pots, each containing a copper plate immersed in a saturated solution of copper sulphate, were used as electrodes. This type of electrode was used to minimize the effects of polarization.

The potential was measured along a line passing through the central electrode. This line was divided into intervals of 20 ft. and a small hole to receive an electrode was prepared at each of the 20-ft. divisions. Non-polarizable electrodes similar to those described above were placed in two of these holes at a distance of 100 ft. from each other, and were connected to a Cambridge "unipivot" potentiometer for the potential measurements. An ammeter was included in the circuit AB (Fig. 1) for the measurement of the current i , which was supplied by a 200-volt battery of accumulators. The distance AB was about 3,500 ft.

At the beginning of an experiment the two potential electrodes were inserted in the holes prepared at a distance of, say $R_1 = 200$ ft., and $R_2 = 300$ ft. from A , and the potential between them measured with the current flowing in the

THE DETECTION OF ROCK SALT BY THE METHODS OF ELECTRICAL SURVEYING¹

BY T. ALTY² AND S. ALTY³

Abstract

Experiments on the detection of rock salt deposits by electrical methods are described. It is shown that these methods give definite indications of the depth of the deposit when the latter is as much as 600 ft. below the surface.

The interpretation of results obtained by the "single electrode probe" method is discussed.

Introduction

During the past summer the methods of electrical surveying have been used in England to determine the depth of rock salt deposits and for other purposes. Since little work on the application of these methods to substances such as salt appears to have been published, the results obtained may be of interest and are given in this note.

The geological structure of the field on which the experiments were performed is comparatively simple and is known in considerable detail from the records of borings made at a number of points on the field. Beneath a surface covering of drift, four or five hundred feet of marl overlie the rock salt, which extends downward for several hundred feet below the marl. The rocks are almost horizontal with a slight dip to the south west; the marl varies in water content but appears to be fairly uniform in structure throughout.

To extract the salt a borehole is usually constructed to extend almost to the bottom of the salt deposit. Water is passed down this hole and, after dissolving the rock salt at the bottom, flows up a return pipe to the surface as brine. In this way a cavity filled with brine is formed at the base of each borehole and this cavity increases in volume as more and more salt is removed.

The experiments described were undertaken with the object of obtaining:

- (a) an estimate of the depth of the upper surface of the rock salt,
- (b) an estimate of the depth of the upper surface of the brine cavities at the base of the boreholes.

Method

The "single electrode probe" method, as described by Eve and Keys (1), was used. In this method an electrode *A* (Fig. 1) is placed in the ground over the point to be explored and another electrode *B* is inserted at a considerable distance from *A*. A battery is then connected to *A* and *B* so that a current flows through the ground between them.

If this ground is uniform and the distance *AB* is sufficiently great, the equipotentials about *A* will be approximately hemispherical as shown in Fig. 1.

Measurements of the total current *i* in the circuit and the potential difference *V* between any two equipotentials of radii *R*₁ and *R*₂, render it possible to

¹ Manuscript received October 30, 1930.

² Professor of Physics, University of Saskatchewan, Saskatoon, Canada.

³ Research Physicist, England.

obtain the average resistivity ρ of the ground between these equipotentials, as follows:

Let $AC = R_1$, and $AD = R_2$.

Then the total resistance between the equipotentials through C and D ,

$$= S = \frac{V}{i} = \int_{R_1}^{R_2} \frac{\rho dr}{2\pi r^2} = \frac{\rho}{2\pi} \left(\frac{1}{R_1} - \frac{1}{R_2} \right)$$

Hence

$$\rho = \frac{2\pi V}{i \left(\frac{1}{R_1} - \frac{1}{R_2} \right)} \quad (1)$$

If, on the ground, a straight line passing through A is divided up into steps and the potential between successive steps is measured, then ρ for each step can be determined from equation (1). Suppose now that a good conductor occurs at the level XY . Then the average resistivity between the equipotentials D and E which intersect

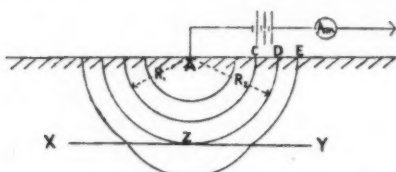


FIG. 1. Diagram illustrating the single electrode probe method of electrical surveying.

the conductor will be decreased and the voltage between D and E will be lower than normal. This decrease in voltage will first appear at a point D such that $AD = AZ$ so that the depth of the conductor may be inferred from the distance AD at which the decrease in voltage, and therefore in ρ , first appears.

In practice therefore the potential difference between successive equal intervals on the ground surface is determined and ρ for each step is calculated by equation (1). The resistivity so obtained is plotted against d , the distance from the potential electrode to the central electrode.

If a good conductor were present below A the resulting graph should show a sudden decrease in ρ at a value of d equal to the depth of the conductor.

Experimental

In our experiments porous pots, each containing a copper plate immersed in a saturated solution of copper sulphate, were used as electrodes. This type of electrode was used to minimize the effects of polarization.

The potential was measured along a line passing through the central electrode. This line was divided into intervals of 20 ft. and a small hole to receive an electrode was prepared at each of the 20-ft. divisions. Non-polarizable electrodes similar to those described above were placed in two of these holes at a distance of 100 ft. from each other, and were connected to a Cambridge "unipivot" potentiometer for the potential measurements. An ammeter was included in the circuit AB (Fig. 1) for the measurement of the current i , which was supplied by a 200-volt battery of accumulators. The distance AB was about 3,500 ft.

At the beginning of an experiment the two potential electrodes were inserted in the holes prepared at a distance of, say $R_1 = 200$ ft., and $R_2 = 300$ ft. from A , and the potential between them measured with the current flowing in the

ground, first in the direction AB and then in the reverse direction BA . This reversal is necessary to eliminate the effects of earth currents and in practice more consistent results were obtained when readings were taken in threes (with the current flowing in the directions AB , BA , AB successively) than when the current was reversed only once.

Having obtained the potential in one position the potential electrodes were each moved 20 ft. further from A and the measurements repeated. This was continued until the distance R_2 (Fig. 1) was about 1,100 ft., ($R_2 - R_1$) being maintained equal to 100 ft. throughout.

From the values of V and i so obtained, the average resistivity ρ was calculated and plotted against R_2 , the distance of the further potential electrode from A . Any sudden decrease in ρ in this graph would then be taken as indicating the presence of a conductor at a depth about equal to R_2 . The reason for selecting R_2 rather than R_1 will be discussed later.

Results

Measurement of the Depth of the Upper Surface of the Rock Salt

Before commencing work in the field the specific resistance of rock salt was determined in the laboratory and found to be about 2×10^6 ohms-cm. The resistivity of the marl was variable but was considerably less than this, so that, on passing from marl to rock salt, the equipotentials are passing from a better to a poorer conductor and an increase in ρ would be expected.

It was found in practice in the field that the average resistivity of the marl, as calculated from equation (1), decreased steadily with increase of depth, *i.e.* with increase of R_2 . The graph of ρ plotted against R_2 was practically linear for values of R_2 less than the depth of the upper surface of the rock salt. At the point corresponding to this depth the graph showed a well defined minimum and the value of ρ increased steadily with further increase in R_2 .

As stated above, this increase in ρ in passing from the marl to the rock salt might be expected since the resistivity of the latter is greater than that of the former. A typical graph is shown in Fig. 2, in which the change in the appearance of the graph on passing from marl to rock salt is well marked.

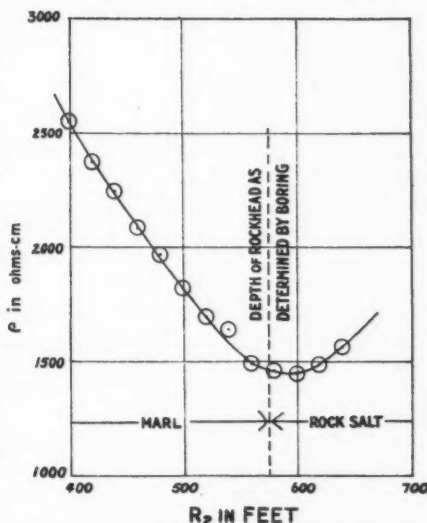


FIG. 2. Diagram showing break in resistivity graph in passing from marl to rock salt.

Experiments were made at different points on the salt field at which the depth of the surface of the rock salt was known from the records of borings. In all cases the value of R_2 corresponding with the minimum value of ρ agreed well with the known depth of the rock salt. The vertical dotted line in Fig. 2 gives the actual depth of the rock-head as determined by boring.

It is because of this agreement that we have throughout plotted ρ against R_2 and taken the depth of any deposit giving a definite break in the $\rho-R_2$ graph as being given by the value of R_2 corresponding to that break.

Measurement of the Depth of the Brine Cavities in the Rock Salt

The cavity at the foot of a borehole is filled with concentrated brine and therefore acts as a good conductor in the surrounding insulating rock salt. The difference of conductivity between brine and rock salt is much more pronounced than between marl and rock salt. This is of course favorable for the detection of the cavities but the advantage so gained has to be set against the disadvantages of their greater depth and limited extent. As they are situated towards the bottom of the rock salt their depth from the surface is very considerable (700-1,000 ft.).

The method used was the same as before, the central electrode being placed at a point 60 ft. to one side of the borehole so as to minimize the disturbance produced by the metal lining tube of the latter.

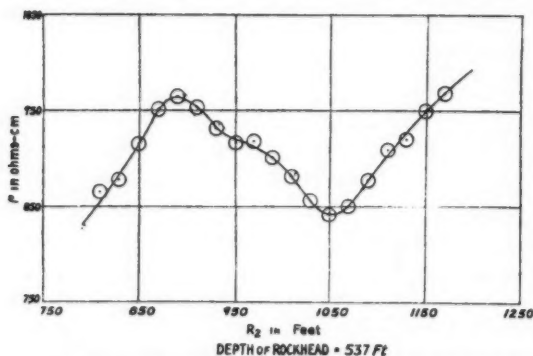


FIG. 3. Resistivity graph obtained with central electrode 60 ft. from borehole.

The potential differences were measured in 20-ft. steps from about $R_2 = 600$ ft. to $R_2 = 1200$ ft. and the graphs plotted as before. The result at one borehole is shown in Fig. 3 from which it will be seen that the resistivity increases with the depth in the rock salt up to the point $R_2 = 860$ ft. at which point there is a sudden decrease. We associate this decrease

with the presence of a conductor at a depth of about 860 ft.

In the rock salt there are occasional bands of marl several feet in thickness so that it was considered advisable to perform an additional set of experiments at some distance from the borehole in order to test whether the conductor indicated above was due to such band of marl or was in reality due to the brine cavity. The central electrode was accordingly moved to a point distant 750 ft. from the borehole and the experiment repeated. At this point the strata were practically identical with those at the borehole so that any effects due to marl bands should be reproduced in this second experiment. The

resistivity graph obtained in this experiment 750 ft. from the borehole is shown in Fig. 4, from which it is clear that there is no indication of a conductor

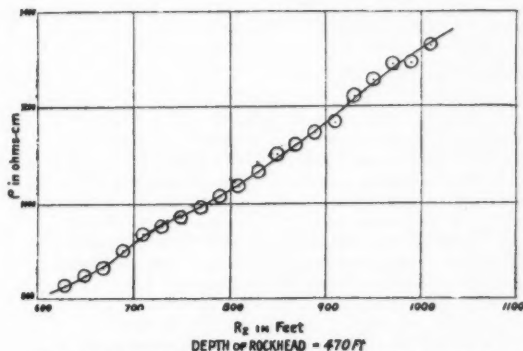


FIG. 4. Resistivity graph obtained with central electrode 750 ft. from borehole.

at this point. Hence it was concluded that the conductor indicated in Fig. 3 was probably the brine-filled cavity at the base of the borehole.

Experiments as described above have been performed at each of three different boreholes and the cavity has been detected in each case, the depths of the upper surface of the three cavities being 860 ft., 770 ft., and

530 ft. respectively. The indication given by the cavity at a depth of 860 ft. is very satisfactory in view of its comparatively small volume.

Summary

It appears from the above results that:

- (a) the depth of the upper surface of the rock salt is obtainable by electrical means,
- (b) the depth of the brine cavity at the foot of the borehole can also be estimated,
- (c) the depth of a deposit giving an indication on the $\rho-R_2$ graph is given by R_2 , the distance from the central electrode to the potential electrode further from it.

Reference

1. EVE, A. S. and KEYS, D. A. Applied geophysics, Cambridge Univ. press, 1929, p. 107.

MOLECULAR ATTRACTIVE FORCES AND THE VELOCITY OF CHEMICAL REACTIONS¹

By C. C. COFFIN² AND O. MAASS³

Abstract

The reactions between hydrogen chloride and α -, β -, and γ -butylene have been investigated in both the liquid and gaseous states. The effect of temperature and concentration of the reactants on the reaction velocities was studied and the reaction products were examined. In the liquid state the γ -isomer reacts rapidly, the α - much more slowly and the β - slowest of all. In the gaseous state at atmospheric pressure only γ -butylene shows a measurable reaction which is bimolecular and probably heterogeneous. The liquid reactions were found to be homogeneous. Where possible the freezing-point curves of the systems were determined in order to ascertain the extent of molecular compound formation. The results obtained bear out the conclusions arrived at from previous work on the effect of molecular attraction upon reaction velocity, and indicate the existence of a catalytic factor peculiar to the liquid state. Suggestions as to the mechanism of such a catalysis are offered.

Introduction

Investigations of the extent of molecular compound formation, and of the velocity of chemical reaction in the liquid state between halogen hydrides and unsaturated hydrocarbons have been carried out in this laboratory (4, 5, 6, 7). The systems studied were hydrogen chloride and hydrogen bromide with ethylene, propylene, acetylene and allylene. The work described here extends this investigation to include the three two-component systems hydrogen chloride and α -, β - and γ -butylene. The effect of temperature and of the concentration of the reactants on the reaction velocity was studied in both the liquid and gaseous states. Where possible the extent of molecular compound formation was estimated by the freezing-point method. The homogeneity of the reactions was tested and the reaction products were examined. The data obtained bear out the ideas advanced in previous papers with regard to the effect of molecular symmetry and molecular attractive forces on the velocity of chemical change. In conclusion the results are discussed from these points of view as well as in connection with modern theories of reaction velocity.

Preparation of Reactants

The hydrocarbons were prepared and purified as described elsewhere (1, 2). The hydrogen chloride, prepared in the usual manner, was dried with phosphorus pentoxide and condensed with liquid air or solid carbon dioxide in vacuo. It was redistilled and the middle fraction was evaporated into the measuring apparatus as required.

¹ Manuscript received November 3, 1930.

Contribution from the Physical Chemistry Laboratory, McGill University.

² Lecturer in Physical Chemistry, Dalhousie University, and holder, at the time, of a fellowship, under the National Research Council of Canada.

³ Professor of Physical Chemistry, McGill University.

Reactants in the Liquid State

Experimental Method

The method of measuring and mixing the reactants has been described in detail in previous papers. Essentially it consists in condensing the gases from known volumes into small glass bulbs cooled in liquid air. From the observed pressure changes the amount of each reactant taken can be calculated. The bulbs were sealed off while surrounded by the liquid air from which they were not removed until plunged into a thermostat at the temperature at which it was desired to carry out the reaction. After the required length of time in the thermostat they were replaced in liquid air where they remained until analyzed. By this method the gases could be manipulated without contact with air or moisture and the amount of each determined to within 1%. Care was taken to have the bulbs as clean and as nearly alike as possible and to make them of such a size, about 3 cc., as to be nearly full of liquid when at the reaction temperature.

The analysis consisted in titrating the remaining hydrogen chloride with 0.1 *N* sodium hydroxide. While still at liquid-air temperature the capillary top was broken off the bulb which was dropped into a suction flask containing distilled water. To the flask, which was tightly stoppered before the contents of the bulb had warmed appreciably, were attached several wash bottles containing distilled water to absorb any escaping hydrogen chloride fumes. After the hydrogen chloride had been absorbed the contents of the bottles and flask were combined and titrated. It was found in preliminary experiments that a much better end-point could be obtained at 0° C. than at room temperature. All subsequent titrations were therefore made in the presence of clean finely-divided ice which, presumably by hindering the hydrolysis of the reaction products, gave a sufficiently definite end-point. Several control experiments in which the mixtures were not allowed to react gave an average agreement of about 1% between the hydrogen chloride taken and that found by analysis.

Velocity of the Reactions

In Fig. 1-A are plotted the results obtained for equimolecular mixtures of hydrogen chloride and α -butylene (curves 2 and 3), and hydrogen chloride and β -butylene (curves 4 and 5) at 0 and 25° C. The previously published (6) curve (No. 1) for the propylene-hydrogen chloride reaction at 0° C. is included for comparison. It will be observed that both butylene reactions are considerably faster at the beginning than that of propylene, but begin to slow up more abruptly as the concentration of hydrogen chloride diminishes. The type of curve, however, is much the same in each case. Moreover the reactions are alike in that they do not proceed to theoretical completion. In the figure the end-points give the per cent hydrogen chloride remaining uncombined at time = ∞ . It will be shown later that this is not due to an equilibrium but to the fact that the butylenes, like propylene, polymerize in the presence of hydrogen chloride. Increase of temperature favors the main reaction more

than the side-reaction as is shown by the greater amount of hydrogen chloride disappearing at the higher temperature. In the case of the system γ -butylene-hydrogen chloride the reaction was so rapid that its velocity could not be determined by the titration method. An attempt was therefore made to follow it

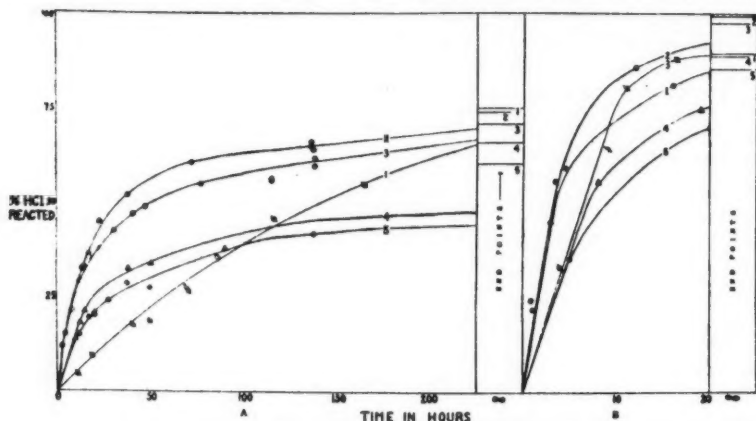


FIG. 1. Rates of reaction between hydrogen chloride and hydrocarbon, (A) in equimolecular and (B) in 2:1 molecular proportions.

Curve 1 = propylene at 0° C.; curve 2 = α -butylene at 25° C.; curve 3 = α -butylene at 0° C.; curve 4 = β -butylene at 25° C.; curve 5 = β -butylene at 0° C.

by means of the heat evolved. It was found that at 0° C. (in a Bunsen ice calorimeter) the reaction is practically instantaneous and that at -78° C. in a carbon dioxide calorimeter in which the gas evolved was measured, it is completed in about one minute. An equimolecular mixture of hydrogen chloride and γ -butylene melts when transferred from liquid air to a carbon dioxide-ether mixture but solidifies again in a few seconds due to the precipitation of the reaction product, tertiary butyl chloride. No side-reaction takes place in this case, the main reaction being presumably too rapid.

A feature common to these reactions is the catalytic effect of excess hydrogen chloride. In Fig. 1-B are plotted the data obtained for the reaction mixture hydrogen chloride-butylene, in molecular proportions of 2:1, at 0 and 25° C. The curve for hydrogen chloride-propylene (in molecular proportions of 2:1) at 0° C. is again included. The per cent hydrogen chloride reacted is calculated on the basis of the amount theoretically required by the hydrocarbon. It will be noted that the differences apparent in Fig. 1-A are in general preserved, all the reactions being accelerated to approximately the same extent, *viz.* from 10 to 15 times that of the equimolecular mixture. That the main reactions are more catalysed than the side-reactions is shown by the greater amount of hydrogen chloride disappearing in each case.

This catalytic effect of excess hydrogen chloride is best shown in the curves of Fig. 2. In this series of experiments mixtures of varying concentrations were made up and allowed to react at the same temperature for equal lengths

of time. The mol fraction of hydrogen chloride in the original mixture is plotted as abscissae while the ordinates represent the per cent reaction calculated on the basis of the reactant present in the smaller proportion. Curve A = α -butylene, 5 hr. at 0° C.; curve B = β -butylene, 5 hr. at 0° C.; curve C = β -butylene, 2 hr. at 0° C. The curve for propylene-hydrogen chloride is very similar to curve A.

It will be observed in each case that above 50 mol per cent hydrogen chloride the acceleration is practically a linear function of the hydrogen chloride concentration. A peculiarity of the β -butylene systems is that excess hydrocarbon also increases the velocity of the reaction, although to a much smaller extent than excess hydrogen chloride. Due to the large experimental errors involved in

determining a relatively small decrease in a high hydrogen chloride concentration the results beyond about 80 mol per cent hydrogen chloride cannot be very accurate. The points in this region however fall sufficiently well upon the extrapolated curves to justify the conclusion that the side-reaction does not take place to any appreciable extent in high hydrogen chloride concentrations.

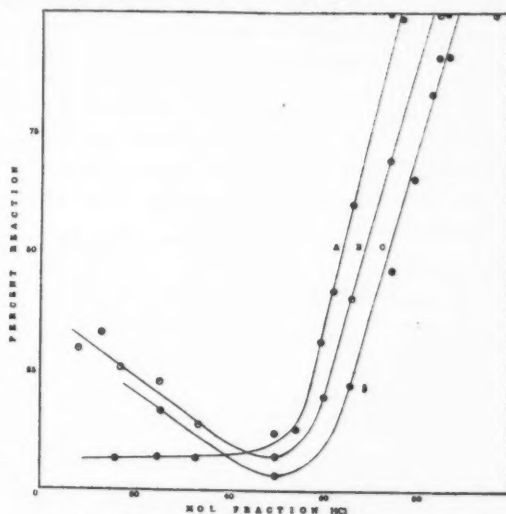


FIG. 2. Effect of varying hydrogen chloride concentration on amount of reaction in equal times. curve A = α -butylene, 5 hr. at 0° C.; curve B = β -butylene, 5 hr. at 0° C.; curve C = β -butylene, 2 hr. at 0° C.

Homogeneity of the Reactions

In order to test the homogeneity of the reactions the following experiments were carried out. In two of four similar bulbs the glass surface in contact with the liquid reactants was increased 200 to 300 times by the addition of small pieces of glass tubing. All four bulbs were filled in the ordinary way with equimolecular quantities of hydrogen chloride and β -butylene and allowed to react for 20 hr. at 0° C. The following results were obtained:

Reaction in bulbs with increased surface	19.6%
	20.0%
Reaction in ordinary bulbs	20.8%
	20.0%
Reaction from velocity curve No. 5 of Fig. 1-A	21.0%

Glass surface has thus no appreciable effect on the velocity of the reaction which takes place homogeneously throughout the liquid. As at least three

separate and distinct preparations of each hydrocarbon and many different lots of hydrogen chloride were used in obtaining the data of Fig. 1 and 2 it is unlikely that the velocity curves are appreciably disturbed by traces of any catalyst introduced as an impurity in the reactants.

The following table summarizes some of the data represented by the curves of Fig. 1-A.

TABLE I
DATA REPRESENTED BY CURVES OF FIG. 1-A.

Hydrocarbon	% Reaction per hour at start		Time to half-value in hr.		End-points hydrogen chloride reacted %	
	25°	0°	25°	0°	25°	0°
Propylene	0.52	0.46	50	80	76	72
α -Butylene	4.0	3.3	18	20	74	71
β -Butylene	1.4	1.2	49	50	66	60
γ -Butylene	100	100	—	—	100	100

Products of the Reactions*

The high vapor pressures (from 20 to 30 atm.) of the reaction mixtures at temperatures at which they will combine at a convenient rate rendered the study of this aspect of the problem somewhat difficult, in that the size of the glass reaction tubes, and hence the amount of product available for investigation, was limited. By the use of long and narrow reaction tubes made of especially thick glass it was found possible to obtain about 50 cc. of the liquid reaction products. A measuring apparatus similar to, but much larger than, that used in filling the small reaction bulbs was employed to handle the relatively large quantities of hydrogen chloride and hydrocarbon required, and a vacuum fractionating apparatus of sufficient capacity to deal with the quantities of liquid involved was constructed. In each case equimolecular quantities of the reactants were taken.

The rapid γ -butylene reaction was carried out at -78°C . in the fractionating apparatus itself. The product was found to be practically pure tertiary butyl chloride (m.p. -26.5°C .) no higher or lower boiling fraction being isolated after many low-pressure distillations. It is interesting to note that the melting point of this compound was found to be considerably higher than that usually given in the literature.

The tube containing the α -butylene-hydrogen chloride mixture was cooled in liquid air and opened after it had remained at 0°C . for 16 days. About 75% of the reaction product was secondary butyl chloride (b.p. 68°C .). Molecular weight and boiling-point determinations as well as bromine absorption and chlorine analysis indicated the remainder to be a mixture of an octyl chloride and an octylene.

*The authors wish to thank Mr. H. S. Sutherland for permission to include in this section material which he is publishing in greater detail elsewhere.

The β -butylene-hydrogen chloride system was allowed to react at 0° C. for 34 days. About 65% of the product was obtained as secondary butyl chloride. The remaining liquid in this case also was found to be very probably a mixture of an octylene and an octyl chloride. These butylene reactions thus resemble that of propylene inasmuch as one product has twice as many carbon atoms as the original hydrocarbon, a fact which necessitates postulating either a termolecular reaction ($1 \text{ HCl} + 2 \text{ hydrocarbon}$) or polymerization of the olefine with subsequent additions of hydrogen chloride (12). That the first step is the formation of a polymer which may or may not add on hydrogen chloride is evinced by the presence of octylenes in the butylene reaction products.

Freezing-point Curves

It was found that, unfortunately, only for the β -butylene-hydrogen chloride system could the complete freezing-point curve be obtained. This is plotted in Fig. 3, Curve A. Curve B represents the only data that could be obtained for the α -butylene-hydrogen chloride system since the main portion of the curve lies below liquid air temperatures.

γ -Butylene and hydrogen chloride react so rapidly at low temperatures that it is impossible to investigate molecular compound formation in this case. All the mixtures that could be frozen showed great tendency to supercool and become cloudy so that exact melting points were very difficult to determine. Some of the points on the curves of Fig. 3 were obtained by the "bulb" method (*i.e.* mixtures were made up in the same way as in the reaction velocity measurements), and some were obtained for mixtures made by condensing quantities of hydrocarbon with a fixed quantity of hydrogen chloride in a small bulb provided with a magnetic stirrer. In each case the bath consisted of petroleum ether cooled with liquid air. Temperatures were measured with a platinum resistance thermometer. As melting points could be determined without keeping the mixtures liquefied for more than a few minutes it is improbable that sufficient reaction could take place to disturb the form of the curve appreciably even in the case of the higher hydrogen chloride concentrations.

The form of curve A gives distinct evidence for the existence of a loose 1:1 compound between hydrogen chloride and β -butylene. This is in agreement with the fact that at higher temperatures reaction takes place with a measurable velocity. From the only part of the α -butylene curve that could be obtained it would seem that a more stable compound exists in this case as would be expected from the greater velocity of this reaction.

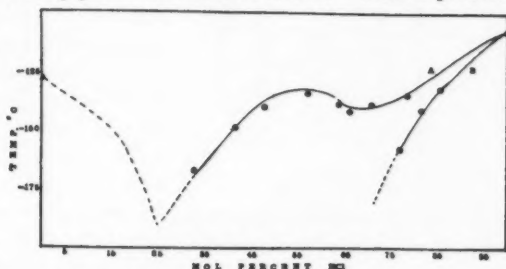


FIG. 3. Freezing-point curves.

- A. β -butylene-hydrogen chloride.
- B. α -butylene-hydrogen chloride.

Reactions in the Gaseous State

Experimental

The apparatus employed in the investigation of the hydrogen chloride-butylene reactions in the gaseous state at pressures up to about one and a half

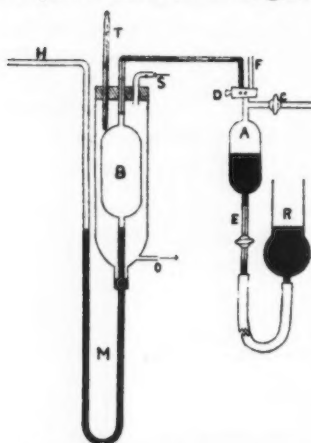


FIG. 4. Apparatus for measuring reaction rate in gaseous state.

atmospheres is shown in Fig. 4. It was operated as follows. The soft glass reaction chamber B (100 cc.) and the measuring bulb A (50 cc.) were thoroughly evacuated through C while B was brought up to the temperature at which it was desired to carry on the reaction. Wet steam could be brought in at S to pass through the pyrex jacket about B and escape at the outlet O. For temperatures other than 100° C., O was sealed off, S was replaced by a reflux condenser, and a liquid of the desired boiling point was boiled in the jacket. When A and B were evacuated tap D was closed and A was filled through C with one of the reactants. The pressure was measured on a manometer, which is not shown, and C was closed. By raising R and opening D the gas was forced by the mercury over into B, D was then closed, R was lowered, and A was filled with

the second component to the desired pressure. When forcing the second gas from A to B the mercury in A was allowed to fill the capillary between the two bulbs before D was closed. Any excess mercury that went through fell down into the manometer M, and the capillary tube remained full. In this way all dead space was eliminated, all parts of the reaction chamber were at the same temperature, and the reactants were in contact with glass and mercury only. By introducing the heavier hydrocarbon last, rapid mixing of the two components was assured. H was connected with a source of vacuum and pressure, a large stabilizing volume, and an open manometer. The volume of B was kept constant throughout the reaction by adjusting the pressure in H so that the mercury remained at the same level on both sides of M. The course of the reaction was thus followed by change of pressure at constant volume. The pressure at zero time was obtained after the reaction by filling B with two volumes of air at the same pressure and temperature at which the reactants had been introduced.

Results

It was found that while hydrogen chloride and γ -butylene reacted in the gaseous state no combination took place between hydrogen chloride and the α - or β -isomer. Several tubes of each of these butylenes mixed with hydrogen chloride remained at 100 cm. total pressure for 40 hr. at 100° C. without any observable decrease in pressure. Mixtures of hydrogen chloride

and hydrocarbon in both equimolecular proportions, and in molecular proportions of 2:1, were tried. These olefines thus resemble propylene in their non-reactivity with hydrogen chloride in the gaseous state (6).

The γ -butylene reaction was studied to a considerable extent. It was found that while the experiments were reproducible within limits in the same tube, the rate varied widely from tube to tube. In a "fast" tube the reaction might be finished in about half an hour while in a "slow" tube it might require several weeks to go to completion. The introduction of a slight excess of either reactant or small amounts of water vapor was found to be without influence on the reaction rate, while the fact that different preparations of hydrogen chloride and hydrocarbon did not give any more consistent or uniform results indicated that no catalyst was being introduced as an impurity. Although the reaction is undoubtedly heterogeneous its rate is not proportional to the extent of glass or mercury surface in contact with the mixture. This was shown by filling one of the slower tubes with glass wool in which was entrained many globules of mercury. The velocity in this tube was indeed somewhat increased but not in the same order of magnitude as the glass or mercury surface.

As it was thought that this catalysis was probably due to traces of the liquid phase, *e.g.* patches of grease on the walls of the reaction chamber, the apparatus was somewhat modified. Stopcocks were eliminated, the whole apparatus was carefully cleaned, mercury was distilled into the manometer M and the inlet capillary was sealed off after filling with the reactants. No success, however, resulted from these attempts to obtain no reaction, although as such tubes were invariably "slow", it is considered that part at least of the observed velocity is due to the presence of traces of some solvent. The extreme rapidity of the reaction in the liquid state and the fact that in the gaseous state at temperatures below the boiling point ($57^{\circ}\text{C}.$) of the reaction product the velocity is very great, lends plausibility to this hypothesis.

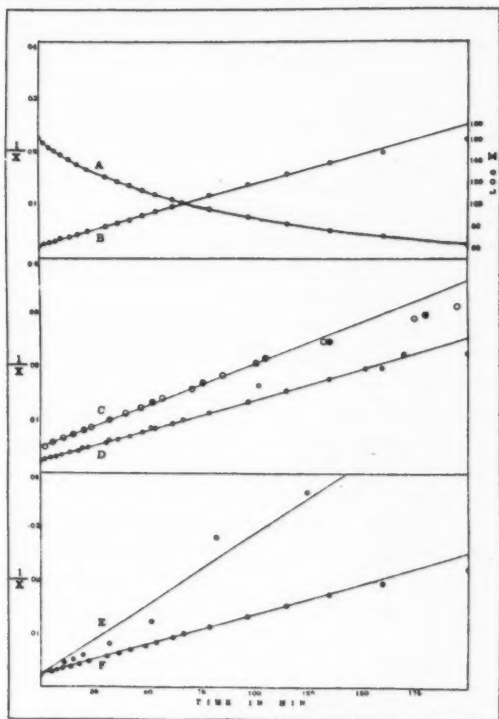


FIG. 5. Rates of reaction in the gaseous state.

In curves A and B of Fig. 5 are plotted the data for obtaining the monomolecular and bimolecular constants of a typical γ -butylene run (No. 15) in a "fast" tube. If equimolecular quantities are taken the partial pressure of one component at any time t is given by the equation,

$$P_{\text{HCl}} = P_{\text{butylene}} = P_t - \frac{1}{2}P_s,$$

where P_t is the total pressure at the time t and P_s is the total pressure at the start. Putting $P_t - \frac{1}{2}P_s = X$ and plotting $\log X$ against time a straight line is obtained if the reaction is monomolecular. If $\frac{1}{P_t - \frac{1}{2}P_s}$ plotted against time is a straight line the reaction is bimolecular. The value of the constant in each case is given by the slope of the line. It is evident from curves A and B that the reaction is definitely bimolecular. The fact that for a monomolecular reaction the time to half-value = $\frac{1}{k} \log 2$, and for a bimolecular reaction = $\frac{1}{Ka}$ (where a = initial concentration) offers another test of the order of the reaction. The following table gives the data of four typical runs in the same tube and at the same temperature, 80°C. The data for obtaining the bimolecular constants are plotted in curves C and D (Fig. 5).

TABLE II
DATA OBTAINED IN FOUR TYPICAL γ -BUTYLENE-HYDROGEN CHLORIDE RUNS, IN THE SAME TUBE
AND AT THE SAME TEMPERATURE, 80°C.

	P_s in cm.	"Half life" in min.
Runs No. 14 and 15 (average) Curve C.	84	22.5
Runs No. 16 and 17 (average) Curve D.	42	40.0

Thus by this test also the reaction is bimolecular. An idea of the temperature coefficient of the reaction may be gained from curves E and F (Fig. 5). Curve E = Run No. 13, 100°C. Curve F = Run No. 15, 80°C.

Discussion

In work which has already been referred to (4, 5, 6, 7), it was found that while propylene and allylene combine at a measurable velocity with hydrogen chloride and hydrogen bromide in the liquid state their more symmetrical homologues ethylene and acetylene are completely unreactive under the same conditions of temperature and concentration. Moreover the freezing-point curves of the reactive unsymmetrical hydrocarbons with these halogen acids gave distinct evidence for the existence in the solution of simple (1:1) molecular complexes. In the case of their more symmetrical and unreactive homologues on the other hand, no such compound formation was observed. These data were considered to emphasize the importance of the part played by molecular attractive forces in determining the velocity of chemical reaction

in such systems and led to the present investigation of the rate of addition of hydrogen chloride to the three simplest isomeric olefines, α -, β - and γ -butylene.

It is of interest to consider briefly the effect of the immediate and self-created environment of such potentially reactive molecules on their rate of combination. If in a two-component system the fields of force surrounding either species of molecules are more completely neutralized by molecules of their own kind than by those of the second component, the effect will be that of a brake on the reaction rate, since it is probable that the acquisition of energy of activation by such "self associated" molecules would be fruitless in furthering the reaction. On the other hand, if the attraction between unlike is greater than that between like molecules the reaction will be accelerated to an extent proportional to some function of the difference of the two forces, since the larger the number of collisions between unlike molecules and the longer their duration, the greater will be the probability of reaction taking place. Thus while some such activation mechanism as postulated by Arrhenius is probably the fundamental factor controlling reaction velocity, its efficiency in systems other than gases at low pressure must be largely dependent on the physical characteristics of the participating molecules themselves and of those of any third component, *e.g.* catalyst or solvent, that may be present. Since in any condensed homogeneous two-component system at least three attractive forces (A to A, B to B and A to B) must be involved, and since they may have any magnitude ranging from that obtaining, for example, in liquid helium to that causing association in a highly polar liquid such as water, it is not surprising that the velocities of apparently very similar chemical reactions should vary so greatly and be so elusive to theoretical treatment.

An estimate of the relative magnitudes of the attractions existing between like molecules is afforded in the case of a series of similar compounds by a comparison of those physical properties, *e.g.* surface tension, melting point and critical temperature, that are known to be influenced by internal cohesive forces. In the same way measurements of deviation from Raoult's law and of the extent of molecular compound formation enable the magnitudes of the attractive forces existing between one species of molecules and a series of others to be compared.

With the object of obtaining such a comparative estimate of their respective molecular attractive forces a number of the physical properties of the three butylenes were determined. These data, which have already been published (1, 2), indicate that an appreciably greater attraction exists between the molecules of β -butylene than between those of either of its isomers. That the β -compound reacts with hydrogen chloride more slowly than do the others is therefore in agreement with the ideas outlined above. That it does react at a measurable velocity conforms with the fact that a certain amount of molecular compound formation occurs at low temperatures.

As most of the physical properties of α - and γ -butylene were found to be very similar it is to be expected that their molecular attractive forces are practically identical, and hence, other things being equal, both isomers should react at the

same rate with hydrogen chloride. Unfortunately no comparison of their attractions for hydrogen chloride molecules can be made since in neither case could the freezing-point curve of the system hydrocarbon-hydrogen chloride be obtained. The fact that γ -butylene, however, reacts so rapidly even at low temperatures points to a type of unsaturation peculiar to the structure



and would lead one to suspect the existence of a well-defined molecular compound. Other examples of the reactivity of this structure are known, *e.g.* trimethylethylene and unsymmetrical methylethylethylene (8) are absorbed in sulphuric acid 20 times as fast as pentene-1 or pentene-2.

The effect of excess hydrogen chloride on the rates of these reactions is of particular interest. That the velocity should increase as abruptly at the equimolecular concentration as indicated by the curves of Fig. 2 points to a radical change in the chemical properties of the solution or in the reaction mechanism at this point. A possible explanation is suggested if the existence of a 1:1 molecular compound is postulated. Thus it might not be impossible for the solution of hydrogen chloride in hydrocarbon to become in a sense "saturated" when equimolecular proportions are reached. At low concentrations of hydrogen chloride the molecules of the latter could be considered as being held by the hydrocarbon in a molecular complex and at concentrations above 50% being free to exert a catalytic effect. Solutions of high hydrogen chloride content could thus be looked upon as solutions of molecular compound in hydrogen chloride. From the known effects of polar solvents on reaction rates it would be expected that hydrogen chloride as a solvent would give rise to some such catalysis.

There are, of course, many objections to such an hypothesis. For instance any molecular compounds that might be found are probably highly dissociated even at the melting point and at the temperature at which the reactions were carried out must be considered as being practically non-existent. Moreover, if the catalytic effect is due to such "free" hydrogen chloride molecules it would seem to follow that an abrupt change in the physical properties of the solution would be evident at the equimolecular concentration. In the case of the system propylene-hydrogen chloride an attempt was made to determine whether or not a physical discontinuity occurred at this point. The vapor (11) in equilibrium with various mixtures of hydrogen chloride and propylene at 78°C. was trapped and analyzed. Over the concentration range examined (45-65% HCl) no sharp break was found in the hydrogen chloride partial pressure curve nor was any discontinuity observed in the vapor pressure curve of the solutions, although a considerable attraction between the two components was indicated by the amount of the deviation from Raoult's law.

Thus, although there seems to be no physical evidence for assuming the hydrocarbon to be saturated with hydrogen chloride in the sense implied in the

above hypothesis, nor any grounds for believing in the existence of molecular compounds at the temperatures at which reaction took place, it must be borne in mind that it is quite possible that the physical and chemical properties of such solutions do not parallel one another as completely as is generally supposed. Purely physical properties, such as vapor pressure and specific heat, are primarily the manifestations of continuous statistical phenomena influenced though they undoubtedly are by the fundamentally chemical forces of molecular attraction. Chemical properties, however, such as reactivity and catalytic power, may involve what might be termed "threshold" effects which give rise to changes and discontinuities that are not reflected in the more physical attributes of the system. An example of the necessity of introducing such a threshold effect is to be found in the conception of activated molecules—molecules whose energy content must be above a certain threshold value before they can take part in the reaction.

Experimental evidence for the idea that discontinuities in the chemical properties of systems may not be manifested in their physical behavior is not lacking. Thus Rodebush and Yntema (10) found that at temperatures at which the vapor pressure of hydrogen chloride was negligible the molecular compound NO:HCl had exactly the same vapor pressure as NO itself, although it was highly colored and very conducting and hence was chemically very different from nitric oxide. The impossibility of detecting molecular compound formation by following the change in such physical properties as viscosity, conductivity, etc. is well known (3). It is therefore considered that for chemical purposes the conception of high concentration mixtures of hydrogen chloride and olefine as solutions of molecular compound in hydrogen chloride is not altogether unwarranted in spite of the fact that physical evidence for such a state of affairs is not forthcoming.

The non-reactivity displayed by these four (including that of propylene) systems in the gaseous state is of particular interest. In the only case where there is room for doubting the absence of a homogeneous gas reaction, *i.e.* in the system γ -butylene-hydrogen chloride, a much smaller velocity is observed than can be accounted for by mere concentration efforts. This can be shown as follows. A certain equimolecular mixture of γ -butylene and hydrogen chloride at 84 cm. initial pressure was found in a "slow" tube to show a pressure decrease of about 3 mm. per hour at 100°C . This reaction, to a great extent at any rate, was probably heterogeneous. Assuming however, for the sake of argument, that it took place homogeneously throughout the gas, the time to half-value would be approximately 70 hr. To bring the mixture to the concentration of the liquid systems a pressure of about 100 atm. would be required. Since the reaction is bimolecular the time to half-value under these conditions (100°C ., 100 atm.) would be $\frac{70 \times 84}{7600}$ or about 0.7 hr. In the liquid state, however, this reaction is instantaneous at 0°C . and is therefore greatly accelerated by some factor other than the concentration of the reactants. Obviously the absence of a measurable gas reaction in the other systems renders the necessity

of assuming the presence of a homogeneous catalyst in the liquid phase still more apparent.

It is suggested that the liquid phase itself fills the role of such a catalyst. The relatively close proximity of the molecules in a liquid, and of course in a highly compressed gas, will bring them more completely within the range of their mutual attractive forces. In the case of polar molecules, where the seat of unsaturation is located at one particular part of the electronic structure, the molecule will not be attracted uniformly by neighboring fields but will reach the minimum potential energy by a definite orientation with respect to the impressed force. Thus throughout the liquid, regional orientation may exist, and as in such regions the rotational energy of a molecule is diminished the chances of fortuitous collision will probably be increased thereby and any reaction in which these molecules are involved will be accelerated. Such orientation must exist in the liquid phase if the transition from the perfect chaos of the gas to the ordered lattice of the crystal is continuous.

Another possible mechanism is suggested by which the liquid phase as such may catalyse a reaction. The molecules in a gas at low pressure exist, except at moments of collision, practically uninfluenced by their neighbors. On the other hand, in a liquid every molecule may be considered to be involved in a perpetual "collision" in that it is continually subjected to stresses and distortions of a magnitude unknown in the vapor phase, except during the relatively rare and momentary phenomena of particularly violent and complicated molecular encounters. It is therefore not unreasonable to suppose that this peculiarity of the liquid state should be conducive to more ready participation in reactions which involve a preliminary rearrangement than obtains in the gaseous phase where sufficiently violent collisions may be events of great rarity. That this idea is in harmony with accepted views of the mechanism of catalytic action in general is brought out in the following statement by Norrish (9). "The catalytic effect of traces of polar substances on gaseous reactions is only one manifestation of a much more general phenomenon, and it may be said that whenever any strong local force can be applied to a molecule so as to distort its stable configuration, that molecule becomes more vulnerable to attack".

It is considered quite possible that the distribution of energy among the interpenetrating fields of force which characterize a liquid may momentarily reach large maxima and so give rise to transient regions of disruptive power sufficient to so distort the normal (*i.e.* when isolated) molecular structure that its stability may be greatly diminished and its reactivity proportionally increased.

Experiments on the rate of these reactions in the gaseous state at high pressure are at present being carried out in an attempt to throw more light on the ideas outlined above.

References

1. COFFIN, C. C. and MAASS, O. Trans. Roy. Soc. Can. 21,III:23-40. 1927.
2. COFFIN, C. C. and MAASS, O. J. Am. Chem. Soc. 50:1427-1437. 1928.

3. ENGLISH, S. and TURNER, W. E. S. *J. Chem. Soc.* 107:774-783. 1915.
4. MAASS, O. and RUSSELL, J. *J. Am. Chem. Soc.* 40:1561-1573. 1918.
5. MAASS, O. and RUSSELL, J. *J. Am. Chem. Soc.* 43:1227-1230. 1921.
6. MAASS, O. and SIVERTZ, C. *J. Am. Chem. Soc.* 47:2883-2891. 1925.
7. MAASS, O. and WRIGHT, C. H. *J. Am. Chem. Soc.* 46:2664-2673. 1924.
8. NORRIS, J. F. and JOUBERT, J. M. *J. Am. Chem. Soc.* 49:873-886. 1927.
9. NORRISH, R. G. W. *J. Chem. Soc.* 123:3006-3018. 1923.
10. RODEBUSH, W. H. and YNTEMA, T. O. *J. Am. Chem. Soc.* 45:332-337. 1923.
11. SIVERTZ, C. Unpublished work.
12. SUTHERLAND, B. P. and MAASS, O. *Trans. Roy. Soc. Can.* 20:III:499-505. 1926.

NOTE ON THE EFFECT OF INTENSIVE DRYING ON THE VELOCITY OF GASEOUS REACTIONS¹BY C. C. COFFIN² AND O. MAASS³

Abstract

Ammonia and carbon dioxide were subjected to intensive drying, with subsequent inhibition of reaction when the gases mixed. Liquefaction of the non-reactive mixture resulted in immediate reaction taking place and the hypothesis is put forward that the "liquid condition" may be looked upon as a catalytic influence.

With the object of determining whether or not gas mixtures (e.g. hydrogen chloride and ammonia) rendered inert by intensive drying would remain so when liquefied, and thus enable the freezing-point curve of the system to be obtained, an attempt was made to dry ammonia and hydrogen chloride to a condition of mutual inertness in the gaseous state. Several trials, however, were unsuccessful and work with this system was temporarily abandoned. The main difficulty arose from the fact that a reaction between the hydrogen chloride and the drying agent, phosphorus pentoxide, absorbed the gas before sufficient time to remove the water had elapsed, and left the tube contaminated with a liquid reaction product. As this liquid was apparently phosphorus oxychloride (1) it, together with water, must have been formed according to some such equation as $P_2O_5 + 6 HCl \longrightarrow 2 POCl_3 + 3 H_2O$. It is obviously useless to attempt to dry a gas in the presence of such a reaction.

Such absorption of hydrogen chloride by phosphorus pentoxide has been mentioned by several investigators* (5, 9) and in the present work proved to be more difficult to eliminate than the reaction between ammonia and phosphorus pentoxide. All precautions that seemed necessary or indeed possible were taken. The phosphorus pentoxide was distilled into the drying tube (all the apparatus was made of pyrex glass) in a slow current of oxygen which was taken from a commercial cylinder, passed through a tube containing red-hot platinized asbestos to eliminate traces of hydrogen, through many wash bottles containing fresh sulphuric acid and through 12 ft. of one-inch glass tubing filled with c.p. phosphorus pentoxide. The pentoxide being distilled was heated by an electric furnace working at 400° C., which could be moved along the pyrex tube. These distillations, each requiring 24 hr., were necessary before the pentoxide reached the final drying chamber, to enter which it had to pass through a section of tube, 2 cm. in diameter and 25 cm. long, containing 40 gm. of spongy platinum heated electrically to a red-heat to oxidize any lower oxides of phosphorus. When sufficient pentoxide had

¹ Manuscript received November 3, 1930.

Contribution from the Physical Chemistry Laboratory, McGill University.

² Lecturer in Physical Chemistry, Dalhousie University, and holder, at the time, of a studentship under the National Research Council of Canada.

³ Professor of Physical Chemistry, McGill University.

* It is of interest to note that the pink HCl mentioned by these investigators was occasionally observed in the course of this work.

collected in the drying chamber the current of oxygen was stopped and the tube was sealed off between the platinum and the pentoxide. The drying tube, through which the oxygen from the pentoxide distillations had been passing, was then heated in a gas furnace to about 400°C . for 12 hr. and kept evacuated to 10^6 mm. with mercury condensation pumps. It was then sealed off from the pumps and the hydrogen chloride admitted through a glass capillary which was broken internally by means of a magnetic hammer. The hydrogen chloride, prepared from c.p. sodium chloride and sulphuric acid, had been previously dried by passing through many wash bottles of sulphuric acid and tubes of phosphorus pentoxide before it was condensed by means of carbon dioxide in vacuo in a tube containing freshly-distilled phosphorus pentoxide. From the tube the required amount was distilled from -100°C . to liquid-air temperature into a bulb attached to the drying chamber and the preliminary drying train was sealed off. On removing the liquid air the hydrogen chloride filled the tube to about atmospheric pressure and immediately began, at first very slowly, to react with the pentoxide. In the later experiments the reaction was followed by a manometer into which previously dried mercury had been distilled. After a few days the remaining hydrogen chloride reacted instantaneously with ammonia, which had been in contact with phosphorus pentoxide prepared as already described. Also a slow absorption of the ammonia by the phosphorus pentoxide invariably occurred. The gases were mixed by magnetically breaking a glass septum separating the two drying chambers. As the reaction of the system $\text{NH}_3 + \text{CO}_2$ to form ammonium carbamate has been observed to be inhibited by drying, it was quite suitable for the desired experiment. Accordingly carbon dioxide was substituted for hydrogen chloride and left in contact with phosphorus pentoxide for three months. Ammonia, previously dried with calcium oxide, was kept in contact with barium oxide for the same length of time. The volume of ammonia was approximately twice that of the carbon dioxide. On breaking the glass seal between the two tubes the gases mixed without precipitation of ammonium carbamate. After interdiffusion had occurred the mixture was condensed in liquid air and the following phenomena were observed. On allowing the bulb in which the mixture was frozen to warm up, most of the carbon dioxide had evaporated by the time the ammonia had liquefied. The carbon dioxide that was left in the bulb immediately reacted with the liquid ammonia to form ammonium carbamate, the excess ammonia boiling off. The ammonium carbamate remained of course a white solid at room temperature. It was possible to observe this several times by raising the liquid air level around the tube. Liquefaction of the ammonia was immediately followed by the solidification of ammonium carbamate. A control experiment in which gaseous carbon dioxide and ammonia, dried by passage through ordinary c.p. phosphorus pentoxide, were mixed resulted in the immediate reaction of the two gases.

* This work was done before the publication of the recent papers by Baker (2) and Bone (4) in which their technique in such experiments is described in greater detail than ever before.

While this experiment indicates the impossibility of utilizing freezing-point curves in the study of molecular compound formation in such systems without still more intensive drying, its result is not without interest from another point of view. That intensive drying will inhibit such reactions in the gaseous state but not so readily in the liquid state has never, as far as the writers are aware, been demonstrated. The fact that the reactions in the liquid state may not be influenced by traces of water suggests that the effect of intensive drying lies really in the removal of all traces of the liquid phase rather than in the elimination of water molecules as such. It is well known that the peculiar polarity of the water molecule and the resulting large surface tension of the liquid gives rise to the formation of charged droplets that are exceedingly difficult to remove, and to liquefaction in the capillaries of the glass surface. Such an explanation of the effect of water on chemical reactivity is in accord with the hypothesis put forward by J. J. Thomson (8, see 3 also) to account for these phenomena, and fits in rather well with the idea suggested elsewhere by the authors (7) that the liquid phase is characterized by a powerful catalytic factor which gives rise to reactions that in the gaseous state do not take place.

Summary

The reaction between carbon dioxide and ammonia was inhibited in the gaseous state by intensive drying. Condensation of this dried gas mixture resulted in a reaction taking place in the liquid formed.

References

1. BAILEY, G. H. and FOWLER, G. J. *J. Chem. Soc.* 53: 755-761. 1888.
2. BAKER, H. B. *J. Chem. Soc.* 1661-1664. 1929.
3. BAKER, H. B. *J. Chem. Soc.* 1051-1055. 1928.
4. BONE, W. A. *J. Chem. Soc.* 1664-1666. 1929.
5. GIAUQUE, W. F. and WIEBE, R. *J. Am. Chem. Soc.* 50: 101-122. 1928.
6. HUGHES, R. E. and SODDY, F. *Chem. News*, 69: 138-139. 1894.
7. MAASS, O. and COFFIN, C. C. *Can. J. Research*, 3: 526-539. 1930.
8. THOMSON, J. J. *Phil. Mag.* 36: 313-327. 1893.
9. TRAMM, H. *Z. physik. Chem.* 105: 356-401. 1923.

A STUDY OF THE RELATIVE VALUE OF HONEY AND SUCROSE IN BREAD MANUFACTURE¹

BY W. F. GEDDES² AND C. A. WINKLER³

Abstract

Honey was substituted for commercial sucrose in various straight-dough bread baking formulae, the doughs fermented for varying times and proofed and baked in the usual manner. No significant difference in loaf volume, flavor, or other bread characteristics could be detected, indicating that honey possesses no superiority over sucrose but is of equal value when compared on the basis of equivalent sugar content. The baking tests were supplemented by studies on the rate of gas production in doughs and also by determinations of the reducing-sugar content of the doughs at the end of the proof period. Rate of gas production was similar and the reducing-sugar content of the doughs were of the same order. A comparison of the results obtained by the different baking formulae indicate the importance of considering the formula in relation to the apparent fermentation tolerance of a flour. No difference was observed in the rate of gas production in partially buffered yeast-honey and yeast-sucrose suspensions of equivalent sugar content prepared in a manner to simulate conditions in fermenting bread doughs. Studies on the rate of inversion of sucrose by yeast showed that the rate of invertase action exceeds the speed of zymase action and indicate that sucrose inversion is not a limiting factor in the rate of gas production in bread doughs. An extension of the market for honey in the baking industry would seem to lie in the direction of increasing its use in sweet goods where its flavor, higher sweetening power and greater hygroscopicity are particularly advantageous—the last in relation to checking. In bread manufacture these properties do not come into play since the relatively low percentage of sugar used is to a large extent removed by fermentation.

Introduction

At a meeting of the Associate Committee on Honey, of the National Research Council of Canada, reference was made to the common belief that the substitution of honey for sucrose in the manufacture of bread results in a more rapid rate of fermentation, and in an improvement in the flavor and keeping quality of the bread.

The basis for the belief that honey might increase the fermentation rate is apparently connected with the fact that the alcoholic ferment—zymase—directly ferments simple sugars such as *d*-fructose and *d*-glucose, of which honey chiefly consists, while the disaccharide sugar must first be hydrolyzed to these sugars by the yeast invertase before being converted into alcohol and carbon dioxide. In other words, in the fermentation of sucrose two reactions are necessary:

1. Sucrose + water $\xrightarrow{\text{invertase}}$ *d*-fructose + *d*-glucose.
2. *d*-fructose and *d*-glucose $\left. \vphantom{\begin{matrix} d\text{-fructose and} \\ d\text{-glucose} \end{matrix}} \right\} \xrightarrow{\text{zymase}}$ ethyl alcohol + carbon dioxide + other metabolic products.

In the case of honey however, essentially only the second reaction is involved and hence fermentation is presumed to be more rapid than with sucrose.

¹ Manuscript received October 18, 1930.

Contribution from the laboratories of the University of Manitoba, Winnipeg, Canada, with financial assistance from the Canadian Co-operative Wheat Producers Limited, and the National Research Council of Canada. Issued as Paper No. 16 of the Associate Committee on Grain Research.

² Professor of Agricultural Chemistry, University of Manitoba, Winnipeg, Canada.

³ Wheat Pool Fellow for Manitoba, 1930, Canadian Co-operative Wheat Producers, Limited.

This reasoning is valid only if inversion proceeds more slowly than alcoholic fermentation, under which circumstances the rate of alcoholic fermentation would be governed by the rate of inversion.

The studies of Balls and Brown (3) on yeast metabolism, however, indicate that the speed of sucrose inversion is not a limiting factor in the rate of alcoholic fermentation of sucrose. These investigators grew cultures of baker's yeast, *Saccharomyces cerevisiae*, in a heavily aerated wort of beet sugar molasses containing ammonium salts as an added source of nitrogen, and monammonium phosphate as an additional food and buffer material. In their experiments, the initial hydrogen ion concentration was approximately pH 6.0, and it changed only slightly as the fermentation proceeded. On seeding with yeast, inversion of sucrose began immediately, accompanied by a loss of total sugar from the medium and the appearance of carbon dioxide and ethyl alcohol. The invert sugar content, however, increased as the fermentation proceeded until a maximum was reached, the concentration-time curves for total and invert sugar finally paralleling each other. Under the conditions of their experiments invert sugar constituted practically the total sugar concentration after the fermentation had proceeded eight hours.

Furthermore, Willstätter and Lowry (17) have shown that the invertase action of yeast may be increased 15 to 20 times or reduced 30 times by suitable treatment without appreciable change in fermenting power and they have demonstrated that it is possible to ferment sucrose directly under conditions which preclude a preliminary hydrolysis by invertase.

However, the conditions prevailing in bread doughs are quite different from those prevailing in yeast-sugar suspensions and, as far as the authors are aware, no investigations are reported in the literature dealing directly with the question of the relative values of honey and sucrose for bread making purposes. The present experiments were undertaken at the suggestion of the Associate Committee on Honey, to ascertain the relative value of these two sources of sugar with a view to a possible increase in the use of honey.

Experimental

A sample of pure unheated Manitoba honey, produced in 1929 in a district where the chief nectar-producing plant was sweet clover, was used in these studies. Moisture and ash content were determined according to the methods outlined by the Association of Official Agricultural Chemists (1). The gravimetric procedure of the A.O.A.C. for the determination of sucrose and invert sugar was followed, but reducing sugars were determined by the procedure recommended by Quisumbing and Thomas (14), which involved the direct weighing of the cuprous oxide. Analysis of the honey gave the following results:

	%	
Moisture	14.2	
Ash	0.22	
Total sugars (as invert)	80.23	<div> { Sucrose 1.76% { Reducing sugars (as invert) 78.38% </div>

I COMPARATIVE BAKING TESTS

First, it was decided to determine the effect of substituting honey for sucrose upon the quality of the bread produced. The flour used in the baking tests was a commercially milled, unbleached, first patent flour (of approximately 50% extraction) milled from hard red spring wheat grown in Western Canada in 1929. The baking method used was that adopted by the Associate Committee on Grain Research, National Research Council of Canada, in their collaborative studies. This method is similar, with certain minor modifications, to the tentative "Basic Standard Procedure" of the American Association of Cereal Chemists as outlined by Blish (4). The basic procedure is followed with respect to the proportions of yeast, salt, and sugar, with the difference that 100 gm. flour on a 13.5% moisture basis (determined by the vacuum oven) is used instead of a 15.0% moisture basis. The absorption is varied in order to produce a dough of the desired consistency, the doughs being mixed in a small Hobart mixer, equipped with two hooks, operated at No. 2 speed for three minutes. The loaves are baked in pans with low sides (top $4\frac{1}{4}$ by $2\frac{3}{4}$ in., bottom $3\frac{1}{8}$ by $2\frac{1}{8}$ in., depth 2 in.). In all other respects the conditions laid down in the basic procedure of the A.A.C.C. are followed. Loaf volume is determined in a measuring device similar to that described by Geddes and Binnington (11).

The method of judging the loaves baked in this study was essentially that adopted by a Conference of Cereal Chemists working under the direction of the Associate Committee on Grain Research. In this method, the characteristics of the bread are scored on a numerical scale, and where a score less than perfect is assigned, a word or letter is appended indicating the type of fault; where no letter is given the fault is not well defined. The following factors were considered in scoring the loaves, and in assigning the key letter.

A. General Appearance

1. Crust color—Perfect score 5.

p = color paler than ideal; d = color darker than ideal.

2. Form—Perfect score 5.

Under this heading are included external characteristics other than crust color.

g = green, or underfermented characteristics; o = overfermented characteristics; f = flat, loaf not well risen; s = shell top.

B. Crumb Character

1. Grain and texture—Perfect score 10.

Grain and texture are considered together, the usual significance of these terms being employed.

c = coarse—thick cell walls; close = small, round cells; o = open—large cells.

2. Crumb color—Perfect score 10.

d = dull; g = grey; y = yellow.

In order to secure a single figure expressive of bread quality an empirical baking score is computed by summing the scores for the bread characteristics weighted in the following manner:

$$\begin{aligned}
 &(\text{Loaf volume} - 400) \times 0.2 = \\
 &\text{Crust color} + \text{form} = \\
 &\text{Crumb texture} \times 3 = \\
 &\text{Crumb color} \times 2 = \\
 &(\text{Absorption} - 60) =
 \end{aligned}$$

Baking Score

A preliminary experiment was first conducted in which 12 loaves in all were baked by the standard method, six with the usual formula using sucrose, and six with the substitution of a weight of honey equivalent in total sugar content to the sucrose ordinarily used, a suitable reduction in the extra water added being made in order to give the same absorption. The mean results given in Table I show that there is no significant difference in any of the bread characteristics recorded, nor could any difference be detected in the flavor of the bread.

TABLE I
THE INFLUENCE OF HONEY ON THE QUALITY OF BREAD BAKED BY BASIC PROCEDURE

Source of sugar	Absorption %	Loaf volume in cc.	Crust character		Crumb character		Baking score
			Color	Form	Color	Texture	
Honey	66.4	627	5.0	4.8	8.0	6.8	98
Sucrose	66.4	628	5.0	4.8	8.0	6.8	98

It is well known to cereal chemists that a single baking method may fail to give a true indication of relative baking quality, variations in the formula or in the baking procedure often revealing wide differences in baking behavior not shown by a single fixed procedure. A more extensive series of baking tests was therefore conducted to determine whether differences in the value of sucrose and honey would become evident when different baking methods were used. These experiments were planned in such a way as to include not only variations in the formula (including two sugar levels), but also different fermentation times. The following formulae were used:

I. Basic Method.

Sugar levels $\begin{cases} 2.5\% \text{—sucrose vs. honey} \\ 4.0\% \text{—sucrose vs. honey} \end{cases}$

II. Bromate Method—Basic formula + 0.001% potassium bromate. Sugar levels and sources of sugar as in I.

III. Malt-Phosphate Method—Basic formula + 0.125% diastatic malt (Lintner value 200°) + 0.05% monammonium phosphate. Sugar levels and sources of sugar as in I.

IV. *Bromate-Malt-Phosphate Method*—Basic formula +0.001% potassium bromate +0.125% diastatic malt +0.05% monammonium phosphate. Sugar levels and sources of sugar as in I.

With each formula, fermentation times of 1.5, 3.0, 4.5 and 6.0 hr. were used, the ratio of the times between the two punches and moulding being 9:4:2. The bakes were conducted in duplicate on different days and where loaf volumes failed to agree within 20 cc. the tests were repeated until the results came within these limits. The results are recorded in Tables II to V inclusive. It will be observed that for a given sugar level, baking formula, and fermentation time, there is no significant difference in any of the bread characteristics recorded, indicating that honey possesses no superiority over sucrose in bread making, but is of equal value when the two are used in amounts yielding equivalent quantities of fermentable sugars. Aside from the question of the relative value of honey and sucrose these results are of considerable interest in connection with fermentation tolerance and will be discussed later.

II. RATE OF GAS PRODUCTION AND REDUCING-SUGAR CONTENT OF DOUGHS MADE WITH HONEY AND SUCROSE

In view of the baking results obtained it seemed of particular interest to determine the rate of gas production, and also the residual reducing-sugar

TABLE II
RESULTS OF COMPARATIVE BAKING TESTS—BASIC METHOD
(MODIFIED TO INCLUDE A 4% SUGAR LEVEL, AND DIFFERENT FERMENTATION TIMES)

Source of sugar	Fermentation time in hr.	Absorption %	Loaf volume in cc.	Crust character		Crumb character		Baking score
				Color	Form	Color	Texture	
2.5% Sugar added in baking formula								
Sucrose	1.5	66	737	4.0d	4.5g	8.0	7.0-c	119
Honey	1.5	66	735	4.0d	4.5g	8.0	7.0-c	118
Sucrose	3.0	66	710	5.0	4.5g	8.0	8.0-c	118
Honey	3.0	66	710	5.0	4.5g	8.0	8.0-c	118
Sucrose	4.5	66	610	4.0p	3.5-os	8.0	6.0 close	90
Honey	4.5	66	591	4.0p	3.5-os	8.0	6.0 close	86
Sucrose	6.0	66	405	3.0p	3.0-of	8.0	3.0 close	38
Honey	6.0	66	409	3.0p	3.0-of	8.0	3.0 close	39
4.0% Sugar added in baking formula								
Sucrose	1.5	66	805	3.5d	4.5g	8.0	7.0-c	132
Honey	1.5	66	794	3.5d	4.5g	8.0	7.0-c	130
Sucrose	3.0	66	755	4.0d	4.5g	8.0	8.0-c	126
Honey	3.0	66	745	4.0d	4.5g	8.0	8.0-c	124
Sucrose	4.5	66	676	5.0	5.0	8.0	8.5	113
Honey	4.5	66	662	5.0	5.0	8.0	8.5	110
Sucrose	6.0	66	529	4.0p	3.5-os	8.0	5.0 close	70
Honey	6.0	66	515	4.0p	3.5-os	8.0	5.0 close	68

TABLE III

RESULTS OF COMPARATIVE BAKING TESTS—BROMATE DIFFERENTIAL
METHOD MODIFIED TO INCLUDE A 4% SUGAR LEVEL, AND DIFFERENT FERMENTATION TIMES

Source of sugar	Fermentation time in hr.	Absorption %	Loaf volume in cc.	Crust character		Crumb character		Baking score
				Color	Form	Color	Texture	
2.5% Sugar added in baking formula								
Sucrose	1.5	66	785	4.0d	5.0	8.0	8.0-c	132
Honey	1.5	66	775	4.0d	5.0	8.0	8.0-c	130
Sucrose	3.0	66	765	5.0	4.5-o	8.0	8.0-o	128
Honey	3.0	66	764	5.0	4.5-o	8.0	8.0-o	128
Sucrose	4.5	66	631	4.0p	4.0-o	8.0	7.0-o	97
Honey	4.5	66	631	4.0p	4.0-o	8.0	7.0-o	97
Sucrose	6.0	66	435	3.5p	3.0-o	8.0	3.0 close	44
Honey	6.0	66	440	3.5p	3.0-o	8.0	3.0 close	46
4.0% Sugar added in baking formula								
Sucrose	1.5	66	815	3.5d	4.5g	8.0	7.0-c	134
Honey	1.5	66	806	3.5d	4.5g	8.0	7.0-c	132
Sucrose	3.0	66	817	3.5d	4.0-o	8.0	7.0-o	133
Honey	3.0	66	807	3.5d	4.0-o	8.0	7.0-o	131
Sucrose	4.5	66	721	5.0	4.0-o	8.0	8.0-o	119
Honey	4.5	66	710	5.0	4.0-o	8.0	8.0-o	117
Sucrose	6.0	66	558	4.0p	3.5-os	8.0	6.0 close	79
Honey	6.0	66	590	4.0p	3.5-os	8.0	6.0 close	86

content of the doughs at time intervals corresponding to those used in the baking tests.

The apparatus and technique devised by Bailey and Johnson (2) for determining the carbon dioxide production of doughs, suggested a ready means of making the measurements. Flour (100 gm.) was mixed, by means of the Hobart mixer, into doughs using the absorption and formulae (with the exception of those containing potassium bromate and, in the case of honey, the malt-phosphate procedure) employed in the baking studies. Determinations of the rate of gas production were made at a temperature of 30° C. using a weight of dough corresponding to 25 gm. of flour (13.5% moisture basis) for each determination. Burette readings were taken at 30 min. intervals for 8.0 hr. The mean results of duplicate determinations are recorded in Table VI.

The identification, separation, and determination of the sugars present in bread doughs are attended with many analytical difficulties. In this study the relative reducing-sugar content of the doughs made with honey and sucrose seemed of major importance and hence reducing sugars only were determined. Flour (200 gm.) was machine-mixed in the manner described for the gas production studies and including the same formulae. After mixing, the doughs

TABLE IV

RESULTS OF COMPARATIVE BAKING TESTS—MALT-PHOSPHATE METHOD (0.125% DIASTATIC MALT+0.05% $\text{NH}_4\text{H}_2\text{PO}_4$) MODIFIED TO INCLUDE A 4% SUGAR LEVEL AND DIFFERENT FERMENTATION TIMES

Source of sugar	Fermentation time in hr.	Absorption %	Loaf volume in cc.	Crust character		Crumb character		Baking score
				Color	Form	Color	Texture	
2.5% Sugar added in baking formula								
Sucrose	1.5	66	771	3.5d	4.5	8.0	7.0-c	125
Honey	1.5	66	755	3.5d	4.5	8.0	7.0-c	122
Sucrose	3.0	66	785	4.0d	4.5	8.0	8.0-c	132
Honey	3.0	66	773	4.0d	4.5	8.0	8.0-c	129
Sucrose	4.5	66	739	4.5d	5.0	8.0	8.0-c	123
Honey	4.5	66	754	4.5d	5.0	8.0	8.0-c	126
Sucrose	6.0	66	609	4.0p	4.5	8.0	7.5	95
Honey	6.0	66	606	4.0p	4.5	8.0	7.5	94
4.0% Sugar added in baking formula								
Sucrose	1.5	66	832	3.0d	4.0g	8.0	7.0-c	136
Honey	1.5	66	810	3.0d	4.0g	8.0	7.0-c	132
Sucrose	3.0	66	791	3.5d	4.5g	8.0	8.0-c	132
Honey	3.0	66	800	3.5d	4.5g	8.0	8.0-c	134
Sucrose	4.5	66	723	4.5d	4.5g	8.0	8.0-c	119
Honey	4.5	66	727	4.5d	4.5g	8.0	8.0-c	120
Sucrose	6.0	66	669	5.0p	4.5g	8.0	8.0-c	109
Honey	6.0	66	650	5.0p	4.5g	8.0	8.0-c	106

were divided into four equal parts by weight, one portion being used for each of the four fermentation times. The doughs were fermented, punched, and panned according to the regular baking procedure. At the end of the 55-min. proof period, 20 gm. dough was weighed out in duplicate and, after quickly cutting into small pieces, dropped into 125 cc. of boiling 50% ethyl alcohol (contained in a 200 cc. Kohlrausch flask) to stop enzymic action. Two grams of calcium carbonate was added to neutralize the acidity and the sugars were extracted by boiling on a steam bath for one hour, a small funnel in the neck of the flask being used as a condenser. After standing overnight, the contents of the flask were made up to volume with neutral 95% ethyl alcohol and thoroughly shaken. After allowing to settle, 100 cc. of the supernatant solution was pipetted into a beaker and evaporated on the steam bath to a volume of approximately 20 cc. The residue was transferred to a 100 cc. volumetric flask, 5 cc. saturated neutral lead acetate solution added, shaken, and, after standing for 15 min., diluted to the mark with distilled water. The solution was then delead with anhydrous sodium carbonate in the usual manner and 50 cc. of the filtrate used for the determination of reducing sugars by the

TABLE V
COMPARATIVE BAKING TEST—BROMATE-MALT-PHOSPHATE METHOD

Source of sugar	Fermentation time in hr.	Absorption %	Loaf volume in cc.	Crust character		Crumb character		Baking score
				Color	Form	Color	Texture	
2.5% Sugar added in baking formula								
Sucrose	1.5	66	800	4.0d	4.5	8.0	8.0-c	134
Honey	1.5	66	785	4.0d	4.5	8.0	8.0-c	132
Sucrose	3.0	66	791	5.0	4.5-o	8.0	7.0-o	131
Honey	3.0	66	790	5.0	4.5-o	8.0	7.0-o	130
Sucrose	4.5	66	602	4.0p	3.5-os	8.0	6.0-close	88
Honey	4.5	66	601	4.0p	3.5-os	8.0	6.0-close	88
Sucrose	6.0	66	431	3.0p	3.0-fo	8.0	3.0-close	43
Honey	6.0	66	441	3.0p	3.0-fo	8.0	3.0-close	45
4% Sugar added in baking formula								
Sucrose	1.5	66	835	3.0d	4.5	8.0	7.0-c	138
Honey	1.5	66	807	3.0d	4.5	8.0	7.0-c	132
Sucrose	3.0	66	820	4.0d	4.5-o	8.0	7.5-o	137
Honey	3.0	66	782	4.0d	4.5-o	8.0	7.5-o	129
Sucrose	4.5	66	755	5.0	4.0-o	8.0	7.0-o	123
Honey	4.5	66	765	5.0	4.0-o	8.0	7.0-o	125
Sucrose	6.0	66	501	4.0p	3.2-o	8.0	5.0-close	64
Honey	6.0	66	511	4.0p	3.2-o	8.0	5.0-close	66

TABLE VI
RESULTS OF MEASUREMENTS OF GAS PRODUCTION IN DOUGHS

Baking formula	Sugar		Gas production, in cc.															
	Source	Amount added %	Interval of time before each reading															
			0.5 hr.	1.0 hr.	1.5 hr.	2.0 hr.	2.5 hr.	3.0 hr.	3.5 hr.	4.0 hr.	4.5 hr.	5.0 hr.	5.5 hr.	6.0 hr.	6.5 hr.	7.0 hr.	7.5 hr.	8.0 hr.
Basic	Honey	2.5	40	59	110	150	192	234	268	308	339	372	402	416	426	435	-	447
Basic	Sucrose	2.5	31	62	112	151	193	235	267	303	339	373	396	430	440	447	454	458
Modified Basic	Honey	4.0	32	57	97	144	188	234	269	314	348	384	413	440	467	490	-	520
Modified Basic	Sucrose	4.0	30	69	113	156	201	254	294	331	368	401	437	462	487	502	514	520
Malt-Phosphate	Honey	2.5	27	74	126	160	200	256	292	340	382	424	463	500	532	563	585	606
Malt-Phosphate	Sucrose	4.0	25	66	116	156	207	251	296	342	380	421	456	490	519	549	582	615

Quisumbing and Thomas procedure. The mean displacement of the solids represented in the 20 gm. dough taken for analysis was calculated from the usual values for flour, salt, yeast and sugar and found to be 8.7 cc. The weight of dough represented in the aliquot taken for analysis was therefore 5.23 gm. The percentage invert sugar corresponding to milligrams of cuprous oxide was obtained by reference to the sugar tables of Quisumbing and Thomas. The mean results, expressed as a percentage of the dough, are given in Table VII.

TABLE VII
PERCENTAGE RESIDUAL REDUCING SUGARS (EXPRESSED AS INVERT) AT END OF PROOF PERIOD

Baking formula	Sugar		% Reducing sugar (as invert) in doughs			
	Source	Amount added %	Fermentation time			
			1.5 hr.	3.0 hr.	4.5 hr.	6.0 hr.
Basic	Honey	2.5	1.08	0.53	0.13	0.10
Basic	Sucrose	2.5	1.04	0.46	0.09	—
Modified Basic	Honey	4.0	1.71	0.87	0.36	0.11
Modified Basic	Sucrose	4.0	1.79	0.78	0.31	0.06
Malt-Phosphate	Sucrose	2.5	1.52	1.00	0.64	0.26
Malt-Phosphate	Sucrose	4.0	2.07	1.32	0.89	0.56

The results of the experiments on gas production and reducing-sugar content of the doughs serve to explain the lack of any significant difference in the baking results obtained when honey is substituted for sucrose in the baking formulae. The rates of gas production of doughs made with the two sources of sugar are not significantly different, and the reducing-sugar levels for the four different fermentation times are of the same order, although, with one exception, the values for honey are slightly higher. If it is assumed that these slight differences are not due to experimental error, which is probably quite high owing to the number of manipulations involved, they may be attributed either to incomplete inversion of sucrose or to the slight diastatic activity of the honey. However that may be, the differences recorded are not reflected in any significant differences in the rate of gas production in the doughs or the quality of the resulting bread.

Considering the baking results with sucrose in conjunction with the gas production and reducing-sugar determinations, the data, considered as a whole, serve to illustrate the influence of the baking formula and method on the apparent fermentation tolerance of a given flour. For purposes of general discussion the results of these studies are presented graphically in Fig. 1 and 2. In Fig. 1 the baking scores are plotted against fermentation time, and in Fig. 2 the rate of gas production and residual reducing sugars at the end of the proof period are also plotted as a function of the fermentation time.

During recent years there has been considerable discussion among bakers and those connected with the milling and baking industry concerning the factors

involved in fermentation tolerance. "Micros" (13) has recently called attention to the different usage of various terms, dealing with this and other associated properties of flour, resulting in considerable confusion. In this discussion the term fermentation tolerance is used in the manner suggested by Swanson (16), who states:

"Fermentation tolerance is taken to mean the time the dough can lay over after it is properly developed, and still produce good bread. It does not refer to the total length of the fermentation period, as this may be longer or shorter with equally good flours and the period would have to be adjusted for the different flours. One hour is a good fermentation tolerance, that is, when a dough is developed so as to produce a good bread after three hours fermentation, it will also give a good bread after four hours."

Researches have indicated that several factors are involved in fermentation tolerance, but much further study is necessary before these can be set down

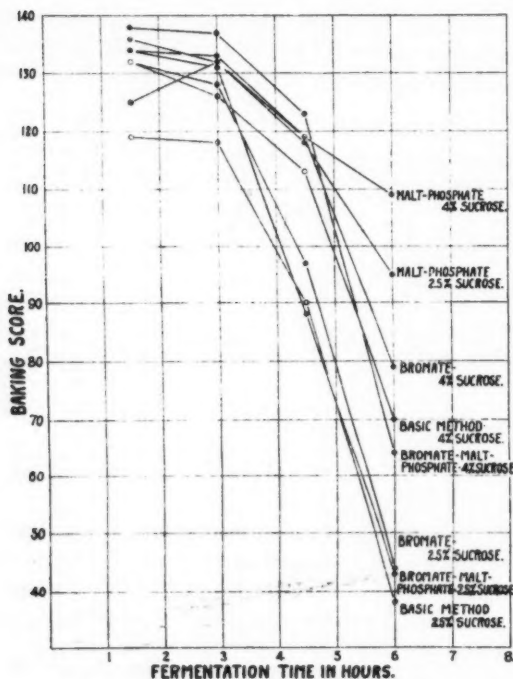


FIG. 1. Showing the relation between baking score and fermentation time for the various bread baking formulae which contained sucrose as the added sugar.

and correlated. It appears, however, from the work already reported that the various factors can be placed in two groups; first, those associated with gas production, and second, those associated with gas retention. Among the factors affecting the rate of gas production may be included water absorption, quantity and quality of yeast, yeast nutrients (such as ammonium salts and phosphates), fermentation temperature, and sugar content of the dough, the last, in turn, depending upon the amount of sugar added in the baking formula, the diastatic activity of the flour, hydrogen ion concentration, and the use of diastatic preparations. On the other hand, factors undoubtedly involved in the gas retaining capacity of a dough include protein content of the flour, and inherent "protein quality", natural aging of flour, chemical aging with oxidizing agents, chemical improvers (such as potassium bromate) which apparently exert their influence by affecting the physico-chemical properties of the dough, hydrogen ion concentration, lipid content and state, and proteases.

Cereal chemists are well aware of the importance of maintaining adequate gas production. The strains of yeast which have been selected and propagated for use in bread manufacture possess high fermenting power for the support of

which a number of substances are required, including soluble nitrogenous compounds, phosphates and fermentable carbohydrates. Flour milled from sound wheat does not contain sufficient fermentable sugars (chiefly sucrose) to properly leaven the dough. Even when sucrose is added in the baking formula the rate of gas production in general tends to fall off in the final stages of fermentation, at the time when it is most needed to distend the dough during the proofing period and the first few minutes in the oven. In such instances a small loaf of poor grain and texture is produced, the loaf possessing a flat taste and pale crust color as a result of low residual sugar content. The fall in sugar level as fermentation proceeds is normally counteracted in part by the natural diastatic activity of the flour or by the addition

of diastatic preparations to the baking formula. With regard to gas retention, the factors are not so well understood.

It is not the intention of the authors to enter into a complete discussion of fermentation tolerance, but merely to indicate that the data obtained in this study serve to illustrate the importance of considering the baking formula in dealing with questions of fermentation tolerance. In this study a "strong" flour was used, and, apart from factors inherent in the flour itself, it is obvious that the rate of gas production as influenced by added sugar, diastatic preparations and yeast nutrients has a profound influence on the apparent fermentation tolerance of the flour. A decrease in the reducing-sugar content below a certain level is accompanied by a falling-off in the rate of gas production which, in turn, is reflected in decreased baking quality. The results

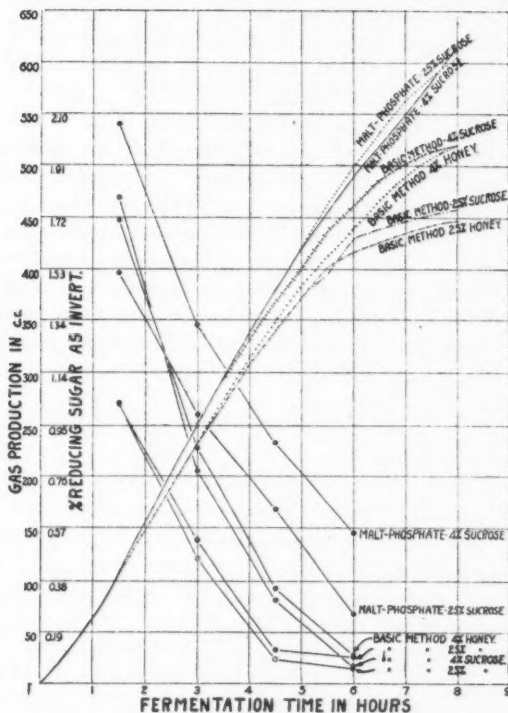


FIG. 2. Showing the rate of gas production in doughs and also the residual reducing sugars at the end of the proof period for different bread baking formulae. Curves with positive slope show rate of gas production. Curves with negative slope show residual reducing sugar content of doughs.

obtained emphasize the importance of diastatic activity in maintaining a uniform rate of gas production, particularly with the longer fermentation times, with a consequent improvement in the baking quality. Blish and Sandstedt (5) have reported that in their experience fermentation tolerance depends more upon the maintenance of adequate gas production than upon the nature of the gluten or gas retaining factor. Callow (6) however, while agreeing that the rate of gas production in the final stages is an important factor in fermentation tolerance, considers that the question of gluten quality or gluten condition cannot be entirely overlooked. These points are of considerable practical importance to the baking trade. Bakers using straight-dough fermentation methods with a formula low in sugar and without diastatic preparations will regard a flour of low diastatic activity as having poor fermentation tolerance. On the other hand, bakers using a sponge method, or a straight-dough method with a formula rich in sugar and malt attach a different meaning to fermentation tolerance, as any deficiency in the diastatic activity of the flour is covered up by the formula used.

III RELATIVE RATES OF GAS PRODUCTION IN YEAST-HONEY AND YEAST-SUCROSE SUSPENSIONS

In addition to the gas-production determinations on fermenting doughs similar tests were conducted on partly buffered yeast-honey and yeast-sucrose suspensions of equivalent sugar concentration. In these experiments it seemed desirable to duplicate, as closely as possible, the conditions existing in bread doughs. Normally, the pH of fermenting bread dough drops, as fermentation proceeds, from an initial value of pH 5.8-6.0 to approximately pH 5.0 and an attempt was made to duplicate this change by partial buffering of the suspensions. In view of the observations of Fales and Nelson (10) on the effect of sodium chloride on invertase action this chemical was also added since it is a constituent of the baking formula. After some preliminary experiments, the following method was adopted which is similar in principle to that recently reported by Cook and Malloch (7) for testing the uniformity of yeast.

Media

1. Sucrose-salt solution—6 gm. sucrose and 2 gm. sodium chloride per 100 cc.
2. Honey-salt solution—As above but substituting for sucrose a weight of honey (3.936 gm.) equivalent in total sugar.
3. *M/20* Buffer solution pH 6.0.
NaOH—KH₂PO₄ buffer.
4. Yeast suspension—3 gm. Fleischmann's yeast per 25 cc. suspension.

The reagents were brought to 30° C. and 25 cc. yeast suspension, 50 cc. sugar, and 50 cc. buffer solution transferred to a flask immersed in a water thermostat maintained at 30° C. and the flask connected to an inverted 100-cc. burette over saturated sodium chloride solution in the manner described by Bailey and Johnson (2). Simultaneous determinations were made on honey and sucrose, the flasks being mechanically agitated and readings of gas production

made at 30-min. intervals for 3.0 hr. The results of one typical experiment are recorded in Table VIII.

TABLE VIII
RATE OF GAS PRODUCTION IN YEAST-HONEY AND YEAST-SUCROSE SUSPENSIONS
(OF EQUIVALENT SUGAR CONCENTRATION) AT 30° C.

Suspension	Gas produced, in cc.					
	Time interval					
	0.5 hr.	1.0 hr.	1.5 hr.	2.0 hr.	2.5 hr.	3.0 hr.
Yeast-sucrose	55	127	222	304	373	380
Yeast-honey	55	127	222	304	373	380

In order to follow the pH change separate flasks were set up from which samples were withdrawn at 30-min. intervals for the electrometric determination of hydrogen ion concentration by means of the quinhydrone electrode. In the particular experiment recorded above the pH values obtained were 5.2, 4.8, 4.4, 4.0, 3.9, 3.9 and 3.9, for the initial period and succeeding 30-min. intervals respectively. This range in hydrogen ion concentration is considerably lower than that in fermenting bread doughs. However, the experiments have been repeated many times covering different pH ranges including 5.8 to 5.0 and the results in all cases indicated no significant difference in the rate of gas production in honey and sucrose suspensions.

IV. RATE OF INVERSION OF SUCROSE BY YEAST

The work of Balls and Brown (3) is not directly applicable to the present situation since their wort was heavily aerated and was merely seeded with yeast. In view of the results reported above it became of interest to trace the change in sucrose concentration and the invert-sugar content of a fermenting sucrose suspension. In order to construct time-concentration curves it was essential to stop yeast action at definite time intervals. Of necessity this must be accomplished by reagents which would not interfere with the subsequent sugar determinations. Toluol, neutral lead acetate, and copper sulphate were tried in different amounts but did not effectively stop yeast action as indicated by gas production measurements. The alkaline tartrate solution of Quisumbing and Thomas (14) and also hydrochloric acid in suitable concentration were found to entirely prevent yeast activity. After considerable preliminary work the following method was finally adopted: 350 cc. sucrose-salt solution, and 350 cc. buffer solution as prepared for the gas production measurements were transferred to a liter flask suspended in the water thermostat at 30° C., and 175 cc. of the yeast suspension at the same temperature rapidly added and the flask agitated mechanically throughout the duration of the experiment.

For the reducing-sugar determination 100 cc. of the test mixture, after a moment of shaking, was immediately withdrawn and added to 100 cc. alkaline

tartrate to stop yeast action, and centrifuged (stop No. 15 International centrifuge) for exactly five minutes to throw down the yeast; 100 cc. of the centrifugate were then drawn into a 250 cc. volumetric flask, made up to the mark with distilled water, and a 50-cc. aliquot used for the determination of reducing sugars by the Quisumbing and Thomas procedure (14). This aliquot represented 10 cc. of the original test mixture and 10 cc. alkaline tartrate, and hence in the sugar determinations 15 cc. alkaline tartrate, 10 cc. water and 25 cc. copper sulphate solution were added in order to furnish the usual conditions required by this procedure.

For the determination of total sugars, 15 cc. of yeast-sucrose suspension was withdrawn from the test mixture, immediately following removal of the portion for the determination of reducing sugars, added to 30 cc. HCl (sp. g. 1.1029) and centrifuged; a 15-cc. aliquot was transferred in duplicate to a 100 cc. volumetric flask, 35 cc. water added and allowed to stand for 24 hr. at room temperature, to allow inversion to take place. This procedure gave the same conditions as outlined by the A.O.A.C. for the acid inversion of sucrose. After neutralizing with anhydrous sodium carbonate and making up to volume, a 50-cc. aliquot was used for the determination of total sugars.

For the determination of hydrogen ion concentration, a 10-cc. portion of the yeast-sucrose suspension was withdrawn and the pH determined electrometrically by means of the quinhydrone electrode.

In view of the well-known destructive action of strong alkalies on sugars it seemed questionable whether the method employed for inhibiting yeast action in the reducing-sugar determinations was justified. To obtain information on this point the following experiment was performed: 400 cc. of sucrose solution (6 gm. per 100 cc.) was inverted by cold acid hydrolysis, neutralized and made up to one litre. Five 100-cc. portions were added to 100 cc. alkaline tartrate, mixed, and allowed to stand for 5 min., the time used in centrifuging in our method; 100 cc. was then transferred to a 250-cc. flask, made up to volume and reducing sugars determined as previously outlined. For the control determinations, 100 cc. of the invert sugar solution prepared above was drawn into a 500-cc. flask, made up to volume and reducing sugars determined on five 50-cc. aliquots. The mean weight of cuprous oxide in the control determinations was 511 mg. and with alkaline tartrate 502 mg. indicating that only slight destruction had taken place.

Determinations of pH, total and reducing sugars were made at 30-min. intervals. The mean results of duplicate determinations recorded in Table IX show the surprising rapidity with which inversion of sucrose takes place. The time required to mix the yeast and sucrose, withdraw an aliquot and add it to the alkaline tartrate was found to be 30 sec. (determined by a stop watch), and yet in this short interval of time some inversion had taken place. At the end of 30 min. inversion is practically complete and indeed, in view of the slight destruction of invert sugar by the method adopted for determining reducing sugars, the sucrose in actual fact may be entirely inverted.

The pH range covered in this experiment is lower than that encountered in fermenting bread doughs. Since the optimal zone for the action of yeast

invertase is between pH 3.5 and 5.5, with the maximal activity at pH 4.5, according to Michaelis and Davidsohn (12), and Sørensen (15), and optimum reaction for zymase (9) lies between pH 6.2-6.8, the results may have been in part due to the higher acidity. The experiment was therefore repeated in the same manner as previously described, with the exception that *M/5* phosphate buffer was used, and portions of the test mixture were removed at 2, 5 and 15 min., in addition to the 30 min. intervals previously employed. The mean results of duplicate determinations are given in Table X and represented graphically in Fig. 3. The results of this experiment again illustrate that the rate of inversion of sucrose by yeast exceeds the rate of zymase action and indicate that sucrose inversion is not a limiting factor in the rate of gas production in fermenting bread doughs.

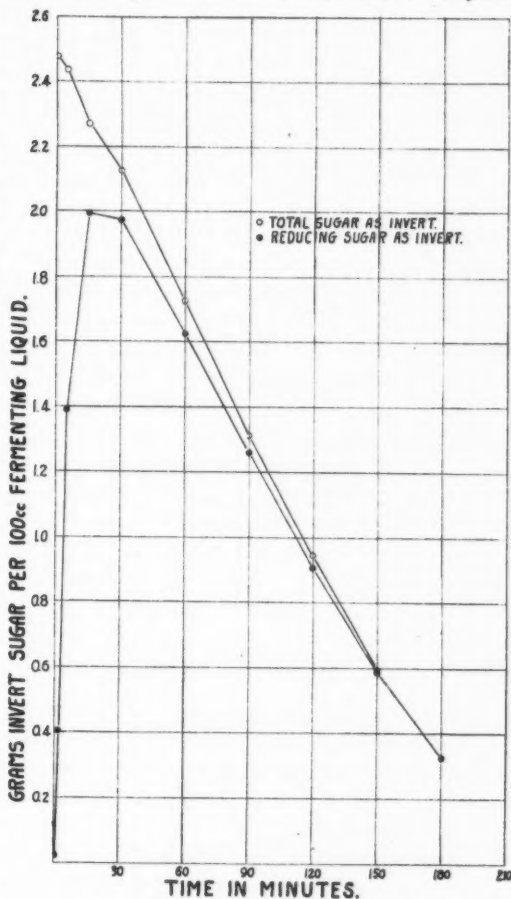


FIG. 3. Showing the rate of inversion of sucrose and the fall in sugar level in partially buffered sucrose-yeast suspensions.

Discussion

The results of these studies require little comment. All the experiments conducted indicate that there is no basis in fact for the claim that honey possesses superiority over sucrose as a substrate for yeast; but it is of equal value when compared on the basis of equivalent sugar content. With honey containing 80% total sugars expressed as invert, this would imply that it must be sold to the baking industry at a pound for pound price 24% less than the prevailing market value of cane or beet sugar. It would also appear that it

TABLE IX
RATE OF INVERSION OF SUCROSE BY YEAST

Determination	Grams per 100 cc. of fermenting suspension						
	Time interval						
	0.5 min.	30 min.	60 min.	90 min.	120 min.	150 min.	180 min.
Total sugars (as invert)	2.55	2.08	1.66	1.28	0.91	0.57	0.32
Reducing sugars (as invert)	0.27	2.01	1.58	1.22	0.90	0.53	0.24
pH	5.2	4.8	4.4	4.0	3.9	3.9	3.9

TABLE X
RATE OF INVERSION OF SUCROSE BY YEAST

Determination	Grams per 100 cc. of fermenting suspension									
	Time interval									
	0.5 min.	2 min.	5 min.	15 min.	30 min.	60 min.	90 min.	120 min.	150 min.	180 min.
Total sugars (as invert)	2.47	—	2.44	2.27	2.13	1.72	1.31	0.94	0.59	—
Reducing sugars (as invert)	0.21	0.40	1.39	1.99	1.97	1.62	1.26	0.91	0.59	0.32
pH	5.9	—	—	—	5.9	5.8	5.7	5.7	5.6	5.6

must compete with cerelose on the same basis. While it is conceivable that certain market conditions might render it necessary to offer certain highly flavored honeys, such as buckwheat, on this price basis, it must be recalled that the color of such honey would preclude its use in the manufacture of white bread.

An extension of the market for honey in the baking industry would seem to lie in the direction of increasing its use in sweet goods such as hard sweets, sugar cookies, and snaps which contain approximately 15%, 38% and 50% sugar respectively on the basis of flour as 100. In many lines of sweet goods, the color of the lower grades of honey is not a deterrent and, aside from flavor, the higher sweetening power of invert sugar as compared with sucrose, together with its greater hygroscopicity, render it particularly valuable for this class of bakery product. In this connection Dunn and Bailey (8) state: "Honey, invert sugar syrup, and dextrose do not produce results in biscuit similar to those produced by sucrose. Whereas biscuit made with sucrose tend to be hard and flat, those made with invert sugar tend to be soft and spongy. The peculiar grain imparted by invert sugar is characteristic and cannot be obtained in any other way. The hygroscopicity of these sugars tends to keep the biscuit soft. This is a very desirable quality, as will be

brought out later. Invert sugar caramelizes at a lower temperature than sucrose, and consequently biscuit containing invert sugar will color more readily than those made with sucrose."

In their extensive investigation of the factors affecting checking in biscuits, Dunn and Bailey (8) have found that checking is progressively decreased as sucrose in the biscuit formula is replaced by invert sugar. They suggest that this beneficial effect may be the result of two causes, namely the softer and more pliable nature of biscuit baked with invert sugar, and also to the fact that biscuit baked with this sugar held more moisture when in equilibrium with the relative humidity of their environment.

In bread manufacture, however, these properties do not come into play since the relatively low percentage of sugar added in ordinary bread-baking formulae is to a large extent removed by fermentation before going to the oven, and the higher oven temperatures used in bread baking would tend to volatilize the odoriferous constituents of honey.

Acknowledgments

The authors wish to acknowledge the financial assistance of the Canadian Co-operative Wheat Producers, Limited, which rendered this work possible. They are also indebted to Mr. S. T. Hadley who, working under a grant from the National Research Council of Canada, conducted the baking tests.

References

1. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Official and tentative methods of analysis. 1925.
2. BAILEY, C. H. and JOHNSON, A. H. Cereal Chem. 1:293-304. 1924.
3. BALLS, A. K. and BROWN, J. B. J. Biol. Chem. 62: 789-821. 1925.
4. BLISH, M. J. Cereal Chem. 5:158-161. 1928.
5. BLISH, M. J. and Sandstedt, R. M. Cereal Chem. 4: 291-299. 1927.
6. CALLOW, R. H. Arkady Review 6:65. 1929.
7. COOK, W. H. and MALLOCH, J. G. Cereal Chem. 7:133-142. 1930.
8. DUNN, J. A. and BAILEY, C. H. Cereal Chem. 5: 395-430. 1928.
9. EULER, H. v. and MYRBACK, K. Z. physiol. Chem. 120: 61-70. 1922.
10. FALES, H. A. and NELSON, J. M. J. Am. Chem. Soc. 37: 2769-2786. 1915.
11. GEDDES, W. F. and BINNINGTON, D. S. Cereal Chem. 5: 215-220. 1928.
12. MICHAELIS, L. and DAVIDSOHN, H. Biochem. Z. 35: 386-412. 1911.
13. "MICROS". Milling. Aug. 24, 1929.
14. QUISUMBING, F. A. and THOMAS, A. W. J. Am. Chem. Soc. 43: 1503-1526. 1921.
15. SÖRENSEN, S. P. L. Biochem. Z. 21: 131-304. 1909.
16. SWANSON, C. O. Cereal Chem. 5:375-385. 1928.
17. WILLSTÄTTER, R. and LOWRY, C. D. Jr. Z. physiol. Chem. 150: 287-305. 1925.

THE BOUND WATER OF WHEAT-FLOUR SUSPENSIONS¹BY R. NEWTON² AND W. H. COOK³

Abstract

The bound-water method was modified for use with flour suspensions and provided a simple means for the direct measurement of the approximate hydration of the colloidal constituents in dilute lactic acid. The average hydration of the dry matter in 15% suspensions was in the region of 40 to 50%, the value being slightly higher in washed suspensions. Starch maintained a hydration close to 30% under all conditions investigated. The prepared proteins, in dilute lactic acid, were hydrated about 85%. The calculated hydration of the proteins as they occurred in the flour was about 100% in unwashed and 200% in washed suspensions.

No significant differences were found by this method in the hydration of strong and weak flours, and it is thought that such differences as may exist are too small to be of major importance as factors in baking quality. The experimental results are harmonized with the facts concerning viscosity and the behavior of bread dough by assuming micellar aggregation of the gluten.

Introduction

The successful use of the bound-water method (18) in measuring the relative hydration of the colloids of plant juices and various prepared sols (17, 19) suggested its possible utility in studying the hydration of the colloidal substances in suspensions of flour in water. The capacity of gluten to absorb a large quantity of water without losing elasticity and coherence is the unique property which makes it so important in bread-making. Alsberg (1), however, has reviewed early experiments which indicate that the absorption of water by flour is as dependent on the starch as on the gluten. The part played by both of these principal components of the flour has been determined in the present experiments.

Because of the importance of the gluten property indicated above, various investigators have attempted to relate it quantitatively to baking strength. Gortner and Doherty (9) measured the absorption by discs of gluten immersed in dilute solutions of various electrolytes, and concluded that gluten from a weak flour had both a lower rate of, and lower maximum capacity for, hydration than gluten from a strong flour. Sharp and Gortner (27) investigated the viscosity of suspensions of flour in water as an index of gluten quality, but while the method at first seemed promising, later investigations by various workers (3, 4, 10, 14, 28) showed that it had no general application in this direction. This is perhaps not surprising when we consider the heterogeneous nature of such a system. Flour and water make not only a colloidal solution of proteins, but also a true solution of salts and sugars and, more than either

¹ Manuscript received November 11, 1930.

Contribution from the Department of Field Crops, University of Alberta, with financial assistance from the National Research Council of Canada. The present paper is being issued as Paper No. 9 of the Associate Committee on Grain Research. It is based upon a thesis presented by the junior author in partial fulfilment of the requirements for the degree of M.Sc. at the University of Alberta, April, 1928.

² Professor of Field Crops and Plant Biochemistry, University of Alberta.

³ Postgraduate student, University of Alberta.

of these, a suspension of starch. Further, Sharp (26) has shown that flour-water mixtures at surprisingly low concentrations follow the laws of plastic rather than of viscous flow.

In the foregoing absorption and viscosity studies, the most important variables were found to be temperature, presence of electrolytes, time and concentration. The bound-water method does not lend itself to an investigation of the effects of temperature on hydration, since the determinations are made at the freezing point, but experiments were designed to test the effect of the other variables noted, using two strong and two weak flours to bring out any relation to baking strength. Experiments were also carried out to ascertain the relative hydration of glutenin, gliadin, and starch.

Adaptation of Bound-water Method

The application of the bound-water method to the study of hydration in plant juices and prepared sols has been discussed in detail elsewhere (17, 19). The method depends upon the cryoscopic determination of the increased concentration of a reference substance (sucrose) in a solution, brought about by the water-binding of the colloids. A similar method was proposed by McBain and Jenkins (16) for measuring the hydration of soap in solution. These authors used chlorides as reference substances, and determined the concentration analytically. Taylor (30) has recently suggested urea as a chemically indifferent reference substance, and developed a highly accurate method for its estimation. The earlier work of Washburn (31) who applied such a method to a study of the hydration of ions, with raffinose determined polarimetrically as the inert substance, escaped our attention until it was referred to by Taylor (30), after our experiments had been completed. Both Washburn and Taylor ascribe the first use of the principle involved to Nernst and his students in 1900. The method here employed is adapted from that of Newton and Gortner (18), who conceived the idea independently and were apparently the first to apply it to biological problems.

The advantages of sucrose as a reference substance were pointed out in the original paper (18). Urea was rejected then because Fischer (7) had shown that it stimulated the hydration of proteins. Dill and Alsberg (6) found later that it peptized gliadin, while Foulger (8) has shown that it also causes the swelling and dispersion of starch. These properties may not be objectionable with inorganic substances and soaps, but they obviously exclude its general use with biological products. Electrolytes are also unsuitable because of their influence on protein hydration. Raffinose is not sufficiently water-soluble for a cryoscopic method.

Cryoscopy as a general method for determining changes in concentration of reference substances is more adaptable, if less accurate, than filtration and analysis. For exact work with pure substances the latter method is to be preferred, but in a heterogeneous mixture, such as a biological fluid, interfering substances make accurate analysis difficult. The freezing-point determination is easily and rapidly performed, and though a high degree of accuracy cannot

be claimed for the estimation of concentration in this way, it is satisfactory where, as in a series of wheat-flour suspensions, we are more interested in the relative than the absolute hydration. The method has been applied to very diverse problems: Richardson and Robertson (23) used it to measure the adsorption of various solutes by charcoal, and Puri (21) applied it to the measurement of "unfree water" in soils.

In adapting to wheat-flour suspensions the method originally devised for plant-tissue fluids, certain modifications of the technique were found advisable. The method called for the addition of enough sucrose to make exactly a molar solution in the total water present, a procedure which necessitated determining the moisture content of the colloidal solution in advance of determining the bound water. As it was inconvenient to make up flour suspensions of an exact moisture content, the method was adopted of making them up to an approximate concentration, and later determining this exactly by evaporating aliquots to dryness. Suitable corrections for the differences in sucrose concentration were made in calculating the bound water. Owing to mechanical difficulties it was found unsatisfactory to determine the freezing point with the starch and undissolved protein present. After experimenting with filtering and centrifuging, the latter procedure was adopted for the removal of solid matter.

In the work on gluten hydration cited earlier (9, 27), the presence of electrolytes and the hydrogen ion concentration had been shown to have a profound effect. The first experiments were therefore planned to discover the best conditions for bound-water determinations with respect to these factors.

EFFECT OF NATURAL ELECTROLYTES

Suspensions of approximately 15% concentration were prepared with four flours, with and without the removal of the natural electrolytes by washing. The washing was done by the method of Sharp and Gortner (27). The bound-water percentages, however, proved to be too small to permit effective comparison of the different flours. They were about 2% for the unwashed flours and still less for the washed samples. The reduction by washing may be explained in part by the removal of dry matter, especially protein, of which about a fourth goes into solution (Table VI). Since the error of the determination is approximately 0.5% bound water, changes indicated by such small figures as those obtained in this experiment must be accepted with reserve. The effect of the natural electrolytes was studied more fully in later experiments. The present experiment showed clearly the necessity of stimulating hydration by changing the hydrogen ion concentration.

EFFECT OF HYDROGEN ION CONCENTRATION

In the experiment on the effect of hydrogen ion concentration the natural electrolytes were washed out, since Sharp and Gortner (27) had found that they caused a greater inhibition of hydration on the acid side than on the alkaline side, and also that a given flour if washed reached more nearly the

same maximum hydration with different acids. Marquis flour suspensions of approximately 15% concentration were used, and the reaction adjusted by adding dilute hydrochloric acid and sodium hydroxide for the acid and alkaline extremes. Intermediate conditions were obtained by the use of phthalate and phosphate buffer solutions. The reagents were allowed to stand in contact with the flour suspensions for 30 min. at 0° C. The results are given in Table I.

TABLE I
BOUND WATER OF WASHED SUSPENSIONS OF MARQUIS FLOUR, DETERMINED WITH
MOLAR SUCROSE CONCENTRATION AT DIFFERENT HYDROGEN ION CONCENTRATIONS

Reagent	Volume of reagent in 110 cc. suspension, in cc.	Hydrogen ion conc'n pH	Bound water %
0.2M HCl	15	2.0	3.9
	5	2.5	3.9
	3.5	2.9	4.3
	2.2	3.8	2.2
0.2M KH phthalate			
+50cc. 0.2M HCl	50	2.4	1.8
+25cc. 0.2M HCl	50	3.2	3.8
(phthalate alone)	50	4.1	2.4
+20cc. 0.2M NaOH	50	5.4	2.0
+50cc. 0.2M NaOH	50	6.5	2.1
0.2M KH ₂ PO ₄			
+30cc. 0.2M NaOH	50	7.2	2.3
+33cc. 0.2M NaOH	50	7.8	2.6
+42cc. 0.2M NaOH	50	9.6	4.4
+50cc. 0.2M NaOH	50	10.0	5.2
0.2M NaOH	3	9.4	3.5
	10	10.4	4.5
	15	10.6	4.1
	25	10.8	2.2

The figures obtained indicate maximum hydration in the regions of pH 3 and pH 10. Sharp and Gortner (27) found maximum viscosity at about pH 3 and pH 11. The present experiment, however, was not regarded as satisfactory, for two reasons: first, it was difficult to obtain consistent readings of the freezing point in the alkaline medium, a disadvantage found also in working with plant juices; second, the viscosity in the region of maximum hydration made it difficult to dissolve all the sucrose in the 30 min. shaking allowed for this process.

The first difficulty showed the desirability of using an acid solution. Lactic acid was adopted as the acidulating agent, since it acts as its own buffer at about pH 3, at which maximum hydration can be expected. Flours differ in their buffer values and hence in the quantity of lactic acid required to bring them to a given acidity. Preliminary experiments with the various flours used showed that 10 cc. of a 5% solution of lactic acid in a suspension of 15 gm. of flour brought to a final volume of 110 cc. insured a reaction of $\text{pH } 3.0 \pm 0.10$.

The problem of dissolving the sucrose was not so easily disposed of. To

increase the time of shaking seemed undesirable, since this would increase the liability of error due to hydrolysis of the sucrose. The use of a lower sucrose concentration seemed the best expedient.

EFFECT OF SUCROSE CONCENTRATION

A comparison was made of the bound water indicated in identical flour suspensions by half-molar and molar concentration of sucrose. The suspensions were acidulated by adding 2 cc. of 5% lactic acid, this amount causing a viscosity which was judged to be as high as would permit the satisfactory solution of the sugar in molar concentration. The time after adding the acid was increased in a few cases, thus taking advantage of viscosity "fall-back" when the original viscosity seemed excessive. One sample nevertheless had to be discarded because the sucrose did not dissolve completely in the time allowed, and the results on the whole were less satisfactory with the higher concentration of sugar. The figures given in Table II show that the half-molar concentration of sucrose indicated bound-water values slightly greater on the average than those obtained by the use of a molar concentration.

TABLE II
BOUND WATER INDICATED IN WASHED FLOUR SUSPENSIONS, ACIDULATED WITH LACTIC ACID, BY HALF-MOLAR AND MOLAR SUCROSE CONCENTRATION

Sample No.	Bound water with M/2 sucrose %	Bound water with M/1 sucrose %
M. 36	4.0	—*
M. 38	3.2	2.6
L.C. 7	4.0	4.8
L.C. 8	4.4	3.8
K. 7	4.9	5.0
K. 8	5.5	5.1
Av. excluding M.36	4.6	4.3

*Suspension too viscous for complete solution of sucrose in given time.

In experiments with gum arabic solutions, Newton and Martin (19) found that a molar concentration of sucrose indicated a higher percentage of bound water than did either 0.5 or 1.5 molar. They noted however that the results with 0.5 molar were not entirely in harmony with theoretical considerations. Increasing the concentration of sugar might be expected to lead to some dehydration of the colloidal particles, and a reduction in bound water. In the present experiments, the half-molar concentration seemed at least as sensitive as the molar as an indicator of bound water, and in ease of solution decidedly more desirable. It remained to investigate the possibility of other errors incident to its use.

Since the freezing-point values, upon which dependence is placed for the measurement of increased concentration due to bound water, would be reduced by the use of a lower sugar concentration, it seemed possible that the per-

centage error would be larger. On the other hand it had been observed in the experiment reported in Table II that it was easier to obtain consistent readings on replicate samples with the lower sugar concentration. To substantiate this observation and obtain some critical data, a series of 49 determinations of the freezing-point depression of half-molar and molar sucrose solutions in distilled water was carried out. For this purpose, 12 samples for each concentration of sugar were weighed and dissolved separately in 30-cc. portions of water, following in this respect the usual bound-water technique. These were subdivided for freezing. The statistical results presented in Table III, therefore, take account of normal errors in weighing as well as in the freezing-point determination.

TABLE III
CRITICAL DATA FOR FREEZING-POINT DEPRESSION
OF HALF-MOLAR AND MOLAR SUCROSE SOLUTIONS

	M/2 sucrose solution Δ	M/1 sucrose solution Δ
Av. 49 determinations	1.036 ± 0.0007	2.179 ± 0.0026
P.E. single determination	0.0046	0.018
Coefficient of variability	0.66	1.22

The results were decidedly in favor of the half-molar concentration, the probable error and coefficient of variability being appreciably lower than for the other. The probable error of a single determination with half-molar sucrose solution corresponds closely to 0.4% bound water. In actual experiments with flour suspensions the replication of the freezing-point determinations would reduce the error considerably, but no significance has been attached to differences of this order.

The use of half-molar sucrose raised the question of possible differences in the hydration of the sugar itself at different concentrations. The evidence discussed by Scatchard (24) indicates that in molar concentration the hydration of sucrose is close to six, but in more dilute solutions is uncertain. The half-molar and molar freezing-point depressions of the stock lot of sucrose used by the present authors are compared in Table IV with those of one lot used by Newton and Martin (19). The latter authors extended the concentration range to include 1.5 molar. In the table are shown also the theoretical depression at a hydration of six and the apparent hydration based upon the experimental values.

The experimental values make it appear that the hydration of the sucrose is greater at half-molar than at molar concentration. Since, however, the behavior of every lot of "c.p." sucrose obtained over a period of years has been slightly different, it seems probable that impurities are in part accountable for the results in Table IV. In the present instance, recrystallizing twice from alcohol reduced the freezing-point depression of the half-molar concentration by only the insignificant amount of 0.003° C. (the mean of eight determinations). The specific electrical conductivity of the original half-molar

TABLE IV
FREEZING-POINT DEPRESSION AND APPARENT HYDRATION
OF SUCROSE AT DIFFERENT MOLAR CONCENTRATIONS

Conc'n <i>M</i>	Theoretical depression at hydration of six	Newton and Martin		Authors	
		Depression found	Apparent hydration	Depression found	Apparent hydration
0.5	0.983	1.036	11.4	1.036	11.4
1.0	2.085	2.120	6.8	2.179	8.1
1.5	3.329	3.436	6.9	—	—

sugar solution was 7×10^{-6} , indicating a practical absence of electrolytes—considerably less, for example, than in a sample of flour washed by the method of Sharp and Gortner. Hence any slight impurities which might be present would probably have little effect on the hydration of the colloids, and since the sucrose was merely a reference substance it seemed permissible to calculate the water bound by the flour from the experimental rather than the theoretical freezing-point depression of the sugar solution. A single lot of sugar was used throughout the investigations. On account of the element of doubt as to the hydration of the sugar itself, however, it was decided to adhere to the assumption that it formed the hexahydrate. If another degree of hydration were assumed, it would change only one constant factor in the calculation and thus introduce a constant percentage correction to the bound-water values, leaving the relative values of a series of colloidal solutions entirely unaffected.

Two errors might result, however, from any large variation in the quantity of water present in different flour suspensions to which a constant quantity of sucrose was added. First, the data show that the freezing-point depression of the sucrose used was not strictly proportional to concentration. Second, the per cent free water in a sucrose solution is the factor kept constant in calculating the water bound by the colloids present, and this would obviously be changed by variations in the total water content. In practice it was found possible to keep nearly all samples within a range of 29 to 31 gm. of water, 30 gm. giving half-molar concentration of sugar. At the limits of this range the maximum deviation of a series of experimentally determined freezing-point depressions from the corresponding depressions found by linear corrections of the half-molar value was 0.004°C . The theoretical free-water percentages when sucrose hexahydrate is formed are 94.4 in 29 gm., 94.6 in 30 gm., and 94.8 in 31 gm. water. Hence it was considered permissible to use linear corrections of the freezing points and to keep the free-water factor constant at 94.6%, or that of half-molar sucrose solution.

To complete the study of the method with respect to the use of half-molar sucrose concentration, the hydrolytic action of the experimental solutions, containing both the natural enzymes of flour and the added lactic acid, was investigated. Samples of unwashed flour were prepared as for a bound-water determination, except that they were allowed to stand an hour in acidulated suspension at 0°C . before being shaken the usual 30 min., and the sucrose

was not added until they had been centrifuged for removal of undispersed matter. The amount by which the freezing-point depression of the extract containing half-molar sucrose, immediately after dissolving the sucrose, was in excess of the sum of the depressions of the extract and half-molar sucrose solution determined separately, is recorded in Table V as the initial Δ_x . It represents the water bound by the substances (e.g. gliadin) which went into solution during extraction of the flour to the extent of nearly 3%. The increased values of Δ_x at later times represent the degree of hydrolysis which had taken place in the extracts containing sucrose during storage in an ice bath. The bound-water equivalents of the increases are given to indicate the magnitude of the errors which might result from delay in completing a bound-water determination.

The results show no measurable hydrolysis in 1 hr., a slight amount in 2.5 hr., and an important amount in 5.5 hr. One hour allows ample time for making a bound-water determination, and samples which had stood longer than this period were discarded. Errors from this source may therefore be neglected.

TABLE V

INCREASE IN FREEZING-POINT DEPRESSION OF ACIDULATED FLOUR EXTRACTS
CONTAINING 0.5 M SUCROSE DURING STORAGE AT 0° C.

Extract No.	Initial	After 1 hr.		After 2.5 hr.			After 5.5 hr.		
	Δ_x	Δ_x	Increase	Δ_x	Increase	Bound water equiv. %	Δ_x	Increase	Bound water equiv. %
1	0.014	0.014	0.0	0.015	0.001	0.1	0.027	0.013	1.2
2	0.018	0.018	0.0	0.024	0.006	0.5	0.034	0.016	1.4
3	0.017	0.017	0.0	0.024	0.007	0.6	0.048	0.031	2.6
4	0.026	0.026	0.0	0.028	0.002	0.2	0.052	0.026	2.2

METHOD ADOPTED

Except in regard to the points specifically mentioned, the method for the determination of bound water used throughout the foregoing preliminary work was identical with that used in the experiments recorded in the following sections. The entire procedure, including the points settled by the preliminary work, will now be outlined.

A paste was prepared from 15 gm. flour and a small quantity of water at 0° C. This was transferred to a graduated cylinder, made up to a volume of nearly 100 cc., then 10 cc. of 5% lactic acid was added and the whole made up to a volume of 110 cc. The graduate was stoppered and shaken vigorously. Duplicate samples were taken quickly (to avoid settling) by filling to overflowing a small graduate cut off at the 34-cc. mark, and triplicate samples of about 8 cc. each were poured into tared drying dishes and covered. The 34-cc. samples contained about 30 gm. of water. They were transferred at once to 100-cc. tared erlenmeyers and weighed, and 5.1336 gm. of sucrose,

ground to pass a 60-mesh sieve, added to each, or enough to make a half-molar concentration in 30 cc. of water. They were then shaken gently in an ice bath on a reciprocating shaker for 30 min. The 8-cc. samples were weighed and dried in a ventilated oven at 90° C. for 24 hr. In the first experiments the samples were transferred to a vacuum oven at the same temperature for the last 12 hr. but it was found that this could be omitted without introducing significant errors. Higher temperatures gelatinized the starch and tended to darken the residues.

At the end of the 30 min. shaking, the two 34-cc. samples and the residue of the original suspension (which remained in the graduate and had been stored without shaking in another ice bath) were transferred to three cooled centrifuge tubes, and whirled long enough to give sufficient supernatant fluid for the freezing-point determinations. These were made by the Beckmann method and carried out at least in duplicate, being repeated if the variation exceeded 0.003° C. An undercooling of 0.5 to 0.7° C. was found to give the best readings with these solutions, the usual correction being made.

The difference between the depression of the supernatant fluid from the residual suspension and of that from the suspension containing sucrose was recorded as Δ_s . From the results of the dry-matter determination, the water present in the 34-cc. samples was calculated, and the corresponding depression of the sucrose, based on its experimental value in distilled water, was recorded as Δ_c . Then $\Delta_s - \Delta_c = \Delta_x$, the excess depression due to increased concentration of sugar as a result of water-binding by the colloids. The per cent bound water = $94.6 \Delta_x / \Delta_s$, in which the factor 94.6 represents the per cent free water in a half-molar solution of sucrose, assuming the formation of the hexahydrate. Since the weight of dry matter and water in the suspensions were both known, the per cent bound water was readily converted to per cent hydration of dry matter.

In succeeding tables where the bound water of washed suspensions is recorded, the modification of the foregoing method consisted in washing the 15-gm. samples of flour by the method of Sharp and Gortner (27) before adding the lactic acid and making up to volume, and in using 32- instead of 34-cc. aliquots, to compensate for the removal of dry matter in washing.

Flours Used

Four flours were selected for use in these studies. Three of these, Marquis, Little Club, and Kubanka were 75% patents, milled in an experimental mill from samples of these varieties grown at Edmonton in 1926. The fourth flour was a standard commercial patent produced by a Canadian milling company for general use. All of these flours were allowed to age for seven months at room temperature before starting the investigation. The samples were analysed for moisture, ash and protein by the usual methods. Glutenin was determined by the method of Blish, Abbot and Platenius (2). The baking data are the result of triplicate tests using 100 gm. of flour on a 13.5% moisture basis, low-sided pans, and a "fixed" method. To remove possible differences

in loaf volume due to lack of diastatic activity, there was added 0.03 gm. of takadiastase per loaf. The results of these determinations are reported in Table VI.

TABLE VI
COMPOSITION OF FLOURS AND RESULTS OF BAKING TESTS

Sample	Moisture %	Ash (dry basis) %	Protein (dry basis) %	Glutenin (dry basis) %	Per cent of total protein removed in washing	Baking data			
						Absorption gm.	Loaf volume cc.	Texture score %	Strength placing
Marquis	11.4	0.47	15.7	6.1	25	65	655	98	1
Com'l									
patent	10.8	0.44	13.3	5.1	30	58	530	100	2
Little Club	11.6	0.55	13.3	5.1	25	59	515	90	3
Kubanka	11.4	0.60	13.9	5.3	20	60	357	88	4
Com'l									
patent	10.6	—	11.6	6.8	—	57	230	85	5
(washed)									

Since in various experiments the flour was washed for the removal of electrolytes, it was considered desirable to obtain some data on the effect of this procedure on the properties of the flour. In the sixth column of the table are given the percentages of the total protein extracted by the washing method of Sharp and Gortner (27). The last sample in the table is the washed commercial patent flour. The wet mass was filtered as dry as possible on a Buchner funnel, then torn up and dried at room temperature in the blast of a desk fan. It was put through a food chopper at intervals during the drying, and finally ground in the reduction roller of a flour mill and sifted through a 10 XX sieve.

The analytical results presented in Table VI show that three of the flours were practically identical in total protein and glutenin content, with the Marquis sample significantly higher in these constituents. The loaf volume shows that the Marquis was decidedly the strongest flour. The commercial patent and the Little Club were practically identical in loaf volume, while the Kubanka was a markedly weak flour, giving small, inferior loaves. The washed commercial patent gave a very poor loaf, owing perhaps to a deleterious effect of the washing and drying procedure on the glutenin, or to the removal of the electrolytes and part of the gliadin, or perhaps in part to both factors. It would seem therefore that the washing procedure is one to be omitted if possible, since it may have an effect on the properties under investigation. The amount of protein removed by washing was highest in the commercial patent. The analyses of this flour after washing show a decrease in total protein and an increase in the percentage of glutenin as would be expected, since gliadin is the more water-soluble of the two proteins.

EFFECT OF TIME ON HYDRATION

The viscosity of a suspension of flour in water, according to Sharp and Gortner (27) and Denham *et al.* (5) falls off rapidly with time. To find whether

this fall-back was due to a change in hydration or to a change in some other property affecting the viscosity determination, a number of acidified suspensions made from washed and unwashed flour samples were stored for varying periods at 0° C. before making the bound-water determinations.

The times recorded in Table VII are taken from the addition of the lactic acid to the actual making of the determination. The technique of the method makes it impossible to get a reading in less than 40 min. The values reported for bound water and average hydration of dry matter are the means of four or more replicates with separately prepared suspensions, but owing to unavoidable errors in this sort of work there are still irregularities in the progression of the figures. It will be observed that the ratios between bound water and hydration are not constant. This is due to varying proportions of the solid and liquid phases in the separately prepared replicate suspensions, which were difficult to adjust accurately.

TABLE VII
EFFECT OF TIME ON HYDRATION OF ACIDULATED FLOUR SUSPENSIONS,
WITH AND WITHOUT NATURAL ELECTROLYTES

Sample	Natural electrolytes present			Natural electrolytes washed out		
	Time in contact with lactic acid	Bound water %	Average hydration of dry matter %	Time in contact with lactic acid	Bound water %	Average hydration of dry matter %
	hr. min.			hr. min.		
Marquis	0 40	4.5	51	0 40	5.7	52
	1 30	5.1	37	1 45	5.2	45
	4 10	4.5	48	3 30	5.8	54
	6 0	4.9	52	10 0	5.2	48
	13 0	5.7	42	23 30	5.6	33
	20 0	4.8	36	30 0	2.9	26
	39 0	4.4	31			
Com'l patent	0 40	4.0	29	0 40	6.1	57
	1 30	5.1	37	1 30	5.2	44
	10 0	4.7	34	3 0	5.6	51
	25 0	5.7	41	7 0	5.0	46
	34 15	5.5	39	25 0	3.6	32
				29 30	3.9	33
Little Club	0 40	7.0	52	0 40	4.6	42
	1 30	5.7	42	1 30	4.7	44
	3 50	5.4	40	3 30	4.3	40
	6 30	5.9	42	12 30	4.5	39
	13 30	5.4	40	18 30	4.7	46
	20 45	6.0	45	21 30	4.7	44
	39 15	4.6	35	25 30	4.3	39
Kubanka	0 40	4.4	34	0 40	5.1	43
	1 30	5.4	38	1 30	4.2	33
	3 45	4.2	36	2 30	4.3	36
	6 15	5.0	34	5 50	4.1	34
	15 0	5.4	39	21 45	3.6	30
	21 15	4.6	33	29 45	3.9	33
	39 30	5.4	36			

These minor variations in concentration affect the bound-water percentages but have little effect on the average hydration of the dry matter, as will be

shown in the next experiment. The latter values therefore provide the best basis for comparison. The effect of time on hydration is partly masked by the irregularities in each series. However, it is quite apparent that while hydration diminishes after prolonged storage, especially in the washed suspensions, there is no immediate fall comparable in magnitude with the fall of viscosity reported by the workers cited above. It would seem therefore that in flour suspensions there is some property other than hydration which contributes to the high initial viscosity of the system.

Comparing the washed and unwashed flours, it is seen that except in the Little Club there is a greater initial hydration in the absence of the natural electrolytes. But on the average, if averaging such figures is permissible, all but the commercial patent show practically the same imbibition, washed and unwashed. It may be that the more noticeable fall of hydration with time in the washed flours is due to the removal of part of the gliadin in the washing process, since this protein may act in a protective role in the original suspension.

Since the average hydration of the dry matter in the washed flour is equal to that in the unwashed flour, in spite of the removal from the former of part of the protein, the most highly hydrated substance, it seems that the hydration of the protein must be greater in the washed flour. Assuming a 30% hydration of the starch (Table IX) and attributing the remaining bound water to the protein, of which a fraction comparable to that shown in Table VI had been removed by the washing, it was calculated that the protein had bound a weight of water in the unwashed flours about equal to, and in the washed flours about double, its own weight. It may therefore be concluded that washing out the electrolytes leads to greater hydration of the remaining protein, a result in harmony with general emulsoid theory.

Regarding hydration and flour strength there is really little to choose among the samples. The decidedly weak Kubanka sample showed lower values than the other flours in the washed series, and was lower than Marquis and Little Club in the unwashed series. The commercial patent, a strong flour, was also low in the unwashed series, but since washing brought it up to the maximum level, it is possible that in the first case the low values may have been due to the kind and amount of salts present.

Effect of Flour Concentration

In the technique which was found best adapted to the determination of bound water, it was inconvenient to make up the flour suspensions to a precise concentration, and when the suspensions were washed it became impossible. For this reason, and also because Sharp and Gortner (27) reported that the slope of the logarithmic viscosity-concentration curve had a relation to strength, being steeper for strong flours, an experiment was planned to determine the effect of concentration on hydration. It was found, however, that the method was not adaptable to a wide range of concentrations. High concentrations became so viscous when acidulated that sucrose would not dissolve satisfactorily even in half-molar concentration in the time allowed. On the other

hand, at concentrations as low as 5% of flour the excess depression was so small as to be seriously affected by the experimental error. Determinations were carried out successfully with unwashed flour up to 18%, and with the more viscous washed flour up to 14% concentration. The size of aliquot taken from the suspension was varied with the concentration to keep the total water content at about 30 gm. The results are given in Table VIII, the concentrations reported being determined as usual by oven-drying.

TABLE VIII
EFFECT OF CONCENTRATION ON THE HYDRATION OF ACIDULATED FLOUR SUSPENSIONS

Sample	Natural electrolytes present			Natural electrolytes washed out		
	Concentration %	Bound water %	Average hydration of dry matter %	Concentration %	Bound water %	Average hydration of dry matter %
Marquis	4.7	2.4	49	5.2	3.0	55
	8.4	3.3	36	7.0	4.0	54
	11.7	5.1	37	7.3	3.7	47
	15.3	6.9	38	9.3	4.8	48
	18.2	8.0	36	10.4	5.2	45
				12.6	5.4	37
Com'l patent	4.5	2.4	50	5.0	4.1	78
	8.5	4.2	45	6.3	4.1	61
	11.6	5.1	37	7.8	4.3	50
	15.4	6.6	36	10.5	5.2	44
	18.1	7.5	36	13.8	6.1	38
Little Club	4.6	1.0	21	5.3	2.4	43
	8.6	4.1	44	6.9	2.7	36
	12.0	5.7	42	7.9	3.5	41
	15.8	6.4	34	9.7	4.7	44
	17.6	7.6	35	9.9	4.8	39
				10.4	5.0	43
				13.2	5.7	37
Kubanka	5.2	1.4	25	5.5	3.7	64
	8.5	4.0	43	7.0	3.9	52
	12.3	5.4	38	8.4	4.3	48
	15.3	6.5	38	11.3	4.2	33
	17.6	7.3	34	12.8	4.2	28
				14.0	5.0	30

These results support the conclusion from the previous experiment that there is no significant difference in the hydration of strong and weak flours. The apparent large differences in hydration of the unwashed strong and weak flours at the lowest concentration may be due to the error previously mentioned. With increasing flour concentration a slight fall in hydration occurs, as observed by Newton and Martin (19) in experiments with various colloids. The short concentration range and the irregularities make it impossible to say whether the hydration follows an adsorption curve. Neither can it be said that the slopes of the hydration-concentration curves of either the washed or unwashed flours have any definite relation to strength. The slope is not sufficiently

pronounced to give cause for regarding as a source of error the minor variations in concentration which occur in the usual bound-water determination. The higher hydration values for the washed samples again demonstrate the inhibiting effect of the natural electrolytes.

Hydration of Starch

While it was assumed that the proteins were the most highly hydrated substances in flour suspensions, and chiefly responsible for differences and changes in viscosity under various conditions, it seemed desirable to measure separately the water bound by both proteins and starch. If this were not

TABLE IX
BOUND WATER AND HYDRATION OF WHEAT-STARCH SUSPENSIONS

Sample	Treatment	Concentration %	Bound water %	Hydration %
Starches dried with alcohol and ether				
Marquis	In contact with lactic acid 1.5 hr.	14.0	4.8	29
	In contact with lactic acid 6 hr.	14.0	4.9	30
Another flour	In contact with lactic acid 1.5 hr.	12.0	4.1	30
	In contact with lactic acid 6 hr.	12.0	3.2	23
Starches not dried with alcohol and ether				
Marquis	Water suspension	12.4	2.7	18
	Lactic acid susp. 1.5 hr.	12.5	3.9	27
Com'l patent	Water suspension	12.0	4.0	30
	Lactic acid susp. 1.5 hr.	11.9	3.8	28
Little Club	Water suspension	11.7	3.2	24
	Lactic acid susp. 1.5 hr.	11.8	4.0	30
Kubanka	Water suspension	11.9	3.9	29
	Lactic acid susp. 1.5 hr.	11.6	4.8	36

done, the criticism made of viscosity measurements with such heterogeneous systems might be levelled also at bound-water determinations. With starch constituting some 80% of the dry weight of the flour, a very moderate degree of hydration would affect importantly the total water bound by the system.

For the first experiment on starch hydration, the starch was prepared from the Marquis flour by the method of Rask and Alsberg (22), drying with alcohol and ether. Its hydration capacity was then determined in dilute lactic acid as used for the flour suspensions. The results for 1.5 and 6 hr. contact with the lactic acid are given in the first part of Table IX. Since the bound-water values were higher than those obtained in the preliminary experiments with unacidulated, unwashed flour suspensions, the experiment was repeated using another starch prepared by the same method from a flour not included in the regular experimental series. The results, given in Table IX, show the same hydration for this starch.

It was then thought that the absolute alcohol and ether treatments used for dehydrating the foregoing samples might have affected the hydration capacity of the starch by extracting some lipoid material. Starches were therefore prepared from all the experimental flours, by kneading them out of the dough and purifying only by repeated differential centrifuging. They were never dried, being weighed directly in the wet condition. For this reason the concentrations shown in the lower part of Table IX are not even percentages as in the case of the dried samples which could be weighed accurately in advance. Their hydration both in water suspension and in dilute lactic acid, as given in the table, were similar to those obtained with the dried starches. Drying apparently has little effect on their later imbibition as measured by this method. The acidulated samples show slightly higher values, but on the whole the figures in the last column of the table indicate that starch has a fairly constant hydration under all the conditions of this experiment.

Alsberg (1) cites Rodewald's calculation made in 1896, that starch imbibes about 36% of water, and holds about the same absolute amount of water in the dough as is held by the gluten. In the present experiment the average hydration of the starches was about 30%. If we assume a protein content of 14% (Table VI) and a starch content of 80% (of dry weight of flour in both cases), it will be seen that to hold as much water as the starch at 30% hydration the protein would have to be hydrated 170%. As calculated in connection with Table VII, this approaches the hydration of the protein found in washed, acidulated flour suspensions.

Hydration of Prepared Proteins

Measurements of hydration in flour suspensions subjected to as little preparatory treatment as possible would seem most desirable, since Svedberg and Sjögren (29) have shown that even the mildest purification process may have a decided influence on the colloidal properties of proteins. Nevertheless, to elucidate further the seat of hydration in the suspensions, a preliminary experiment was carried out on a sample of gliadin and glutenin prepared by Osborne's

method (20). Both proteins were dissolved and precipitated three times to effect purification. They were dehydrated with absolute alcohol and anhydrous ether, and ground to pass a 100-mesh sieve.

TABLE X
BOUND WATER, HYDRATION AND VISCOSITY OF ACIDULATED PROTEINS

Protein	Concentration %	Bound water %	Hydration %	Viscosity time of flow (water = 12.2) sec.
Gliadin	1.3	1.2	94	18.0
	3.2	2.4	73	20.0
	4.9	3.4	67	30.4
	6.5	4.8	70	43.5
	8.8	7.8	81	76.0
Glutenin	1.3	1.5	110	—
	3.1	2.3	72	—
	4.8	4.0	80	—
	6.8	6.6	91	—

The hydration of these proteins in various concentrations, in dilute lactic acids as used for the flour and starch suspensions, is shown in Table X. The gliadin swelled and then dispersed completely in these solutions, after which the determinations were carried out immediately. The glutenin, however, swelled to its maximum with practically none going into true colloidal solution. All glutenin concentrations were shaken five hours in an ice bath before determining the bound water. The highest concentration of this protein had to be abandoned, because the mixture was too thick and unmanageable. The viscosity of the gliadin solutions is also shown in the table, but not that of the glutenin because of its failure to disperse. An Ostwald viscosimeter with a water time of 12.2 sec. was used, and the readings are given in seconds rather than relative or absolute units, since there was not sufficient material for making specific gravity determinations.

The hydration of these prepared proteins is not expected to indicate their normal imbibition in flour suspensions or in bread dough. The preparation apparently impaired their imbibitional properties, since their hydration in these solutions was in the region of 85%, as compared with about 200% in similarly acidulated washed flour suspensions. The hydration here as in the flour suspensions probably decreases slightly as the concentration increases, though the values are too irregular to warrant a definite statement. It is interesting to note that the glutenin is, if anything, more highly hydrated than the gliadin, notwithstanding that the former did not disperse. Similar relationships have been found in other colloids(19). The capacity of the glutenin to retain its coherence while absorbing large quantities of water is undoubtedly of great importance in the colloidal behavior of dough.

Discussion

The elasticity and coherence of strong gluten are difficult to explain in terms of hydration rates and capacities alone. Loeb (13) concluded that the protein molecules in gelatin sols were aggregated into micellae which entrapped relatively large quantities of water and so increased the bulk of the gelatin and the viscosity of the sols. McBain (15) showed that the decreased viscosity of such a system after shearing could be explained by the breaking up of the aggregates. Scott Blair, Watts and Denham (25) extended Loeb's conception to flour suspensions, but concluded (5) that viscosity fall-back was not due to either repeated shearing or proteolysis, but probably to syneresis.

Differences in gluten which would affect its strength can be visualized more easily on the basis of a "brush heap" structure made up of interwoven micellae, than if we take Hatschek's view (11, 12) and regard a colloidal solution as containing independent particles each surrounded by a thick film of solvent, which in effect increases the particle size and so also the viscosity. On the latter view it is difficult to reconcile hydration with the maintenance of coherence and elasticity. Moreover, the experiments now reported show no great difference in the hydration of strong and weak flours, and the hydration was fairly constant over quite long periods, in this respect differing sharply from viscosity. It was further noted that the acidulated samples stored in an ice bath showed no evidence of settling during the first six hours, but after that the solids settled quite rapidly.

If the micellar structure be accepted, strong gluten, even though no more hydrated than weak gluten, may be pictured with more aggregation which entraps more water and leads to a higher adsorption in dough and higher initial viscosity in flour suspensions. Denham, Scott Blair and Watts (5) found that the rate of viscosity fall-back in flour suspensions increased with concentration and was to some extent related to flour strength. Both these factors, on the view now put forward, might be expected to increase the number of particle junctions and the probability of their separation under the peptizing influence of the weakly acid medium. The syneresis postulated by these authors, and which doubtless contributed to the eventual settling of our suspensions, might be regarded either as the release of entrapped water by a decrease in aggregation or as a squeezing out of water by shrinkage of the micellae. In either case true hydration, or adsorption of water on the colloidal surfaces, would not be affected. That it is true hydration which is measured by the bound-water method seems likely, since no decrease was found paralleling viscosity fall-back.

A gluten structure consisting of interwoven micellae entrapping the dispersion medium makes both the coherence and elasticity of dough comprehensible. Such a mass will arrange itself to give a minimum of surface energy. On distortion the micellar structure will be disarranged, increasing the surface between the two phases. If the distorting force is small and of short duration the increased surface energy will cause the mass to resume its initial shape. If the force is large or of long duration, some of the dispersion

medium will be squeezed out of the micellae and the mass will not recover its original form. These are just the properties of gluten or bread dough.

Gluten quality may therefore be attributed to other properties than the hydration rates or capacities of its proteins. While the importance of their imbibitional capacity must not of course be overlooked, the very fact that the prepared glutenin and gliadin showed approximately the same hydration associated with coherence in the one case and dispersion in the other, indicates the necessity of considering structure as well as hydration in connection with the properties of gluten. A discussion of the respective roles of the components of gluten is, however, outside the scope of this paper.

No great accuracy is claimed for the bound-water method, and there may be real differences in the hydration of strong and weak flours which it did not detect, but it seems probable that the differences are too small to be regarded, of themselves alone, as significantly affecting the baking quality of these flours. The method has provided a simple means of estimating the approximate hydration of the main constituents of flour suspensions. The proteins were hydrated to the extent of about 100% in unwashed and 200% in washed flours; with starch the hydration was about 30% under all conditions investigated. Considering the relative quantities of these constituents in the flour, it appears that the starch must bind as much water as the proteins.

References

1. ALSBERG, C. L. Starch in flour. *Cereal Chem.* 4: 485-492. 1927.
2. BLISH, M. J., ABBOT, R. C. and PLATENIUS, H. The quantitative estimation of glutenin in wheat flour. *Cereal Chem.* 4: 129-135. 1927.
3. BLISH, M. J. and SANDSTEDT, R. M. Viscosity studies with Nebraska wheat flours. *Cereal Chem.* 2: 191-201. 1925.
4. COLEMAN, D. A., DIXON, H. B. and FELLOWS, H. C. A comparison of some physical tests for determining the quality of gluten in wheat and flour. *J. Agr. Research*, 34: 241-264. 1927.
5. DENHAM, H. J., SCOTT BLAIR, G. W. and WATTS, G. Notes on the use of Ostwald viscometers for flour suspensions. *Cereal Chem.* 4: 206-220. 1927.
6. DILL, D. B. and ALSBERG, C. L. Preparation, solubility and specific rotation of wheat flour gliadin. *J. Biol. Chem.* 65: 279-304. 1925.
7. FISCHER, M. H. *Oedema and Nephritis*. 2nd ed. New York, 1915.
8. FOULGER, J. H. The solvent power of urea solutions. *Med. Bull., Univ. of Cincinnati*, 3: 46-47. 1924.
9. GORTNER, R. A. and DOHERTY, E. H. Hydration capacity of "strong" and "weak" flours. *J. Agr. Research*, 13: 389-418. 1918.
10. GREWE, EMILY and BAILEY, C. H. The concentration of glutenin and other proteins in various types of wheat flour. *Cereal Chem.* 4: 230-247. 1927.
11. HATSCHEK, E. The viscosity of colloidal solutions. *Colloid Chemistry* (Ed. by J. Alexander), 1: 738-750. New York. 1926.
12. HATSCHEK, E. The apparent viscosity of colloidal solutions. *J. Phys. Chem.* 31: 383-392. 1927.
13. LOEB, J. *Proteins and the theory of colloidal behaviour*. 2nd ed. New York. 1924.
14. MALLOCH, J. G. The effect of irrigation on quality in wheat. Univ. of Alberta, M.Sc. thesis (unpublished). 1926.

15. MCBAIN, J. W. The apparent viscosity of colloidal solutions and a theory of neutral colloids as solvated micelles capable of aggregation. *J. Phys. Chem.* 30: 239-247. 1926.
16. MCBAIN, J. W. and JENKINS, W. J. The ultra-filtration of soap solutions: sodium oleate and potassium laurate. *J. Chem. Soc.* 121: 2325-2344. 1922.
17. NEWTON, R. Colloidal properties of winter wheat plants in relation to frost resistance. *J. Agr. Sci.* 14: 178-191. 1924.
18. NEWTON, R. and GORTNER, R. A. A method for estimating hydrophilic colloid content of expressed plant-tissue fluids. *Botan. Gaz.* 74: 442-446. 1922.
19. NEWTON, R. and MARTIN, W. M. Physico-chemical studies on the nature of drought resistance in crop plants. *Can. J. Research*, 3: 336-427. 1930.
20. OSBORNE, T. B. The proteins of the wheat kernel. *Carnegie Inst. Wash. Pub.* 84. 1907.
21. PURI, A. N. The hypothesis of "unfree water" in soils. *Agr. J. India*, 29: 318-324. 1929.
22. RASK, O. S. and ALSBERG, C. L. A viscosimetric study of wheat starches. *Cereal Chem.* 1: 7-26. 1924.
23. RICHARDSON, H. L. and ROBERTSON, P. W. The cryoscopic method for adsorption. *J. Chem. Soc.* 127: 553-556. 1925.
24. SCATCHARD, G. The hydration of sucrose in water solution as calculated from vapor-pressure measurements. *J. Am. Chem. Soc.* 43: 2406-2418. 1922.
25. SCOTT BLAIR, G. W., WATTS, G. and DENHAM, H. J. Effect of concentration on viscosity of flour suspensions. *Cereal Chem.* 4: 63-67. 1927.
26. SHARP, P. F. Wheat and flour studies V. Plasticity of simple flour-in-water suspensions. *Cereal Chem.* 3: 40-56. 1926.
27. SHARP, P. F. and GORTNER, R. A. Viscosity as a measure of hydration capacity of wheat flour and its relation to baking strength. *Minn. Agric. Exp. Sta. Tech. Bull.* 19. 1923.
28. SMITH, E. E. Viscosity and baking quality. *Cereal Chem.* 2: 177-190. 1925.
29. SVEDBERG, T. and SJÖGREN, B. The molecular weights of serum albumin and of serum globulin. *J. Am. Chem. Soc.* 50: 3318-3332. 1928.
30. TAYLOR, MILLICENT. A highly accurate method for the analysis of urea. *J. Am. Chem. Soc.* 50: 3261-3265. 1928.
31. WASHBURN, E. W. The hydration of ions determined by transference experiments in the presence of a non-electrolyte. *J. Am. Chem. Soc.* 31: 322-355. 1909.

al
7.
ce
e.
t
t
7.
9.
t.
t.
r-
y
t
3.
n
t.
n

